https://doi.org/10.5194/egusphere-2023-1915
Preprint. Discussion started: 12 September 2023

Calibration methods for laser ablation Rb–Sr geochronology: comparisons and recommendation based on NIST glass and natural reference materials

Stijn Glorie[1*], Sarah E. Gilbert[2], Martin Hand[1], Jarred C. Lloyd[1]

[1] *Department of Earth Sciences, University of Adelaide, SA 5005, Australia.*

[2] *Adelaide Microscopy, University of Adelaide, SA 5005, Australia.*

Correspondence to: Stijn Glorie (stijn.glorie@adelaide.edu.au)

Abstract

In-situ Rb–Sr geochronology using LA-ICP-MS/MS technology allows rapid dating of K-rich minerals such as micas (e.g. biotite, muscovite, phlogopite) and K-feldspar. While many studies have demonstrated the ability of the method, analytical protocols vary significantly and to date no studies have provided an in-depth comparison and synthesis in terms of precision and accuracy. Here we compare four calibration protocols based on commonly used reference materials for Rb–Sr dating. We demonstrate that downhole fractionation trends (DHF) for natural biotite, K-feldspar and phlogopite contrast with that for the commonly used Mica-Mg nano-powder reference material. Consequently, Rb–Sr dates calibrated to Mica-Mg can be up to 5% inaccurate and the degree of inaccuracy appears to be unsystematic between analytical sessions. Calibrating to Mica-Mg also introduces excess uncertainty that can be avoided with a more consistent primary calibration material. We propose a calibration approach involving NIST-610 glass as the primary

https://doi.org/10.5194/egusphere-2023-1915
Preprint. Discussion started: 12 September 2023

reference material (RM) and a natural mineral with similar DHF characteristics to the analysed samples as secondary RM to correct for matrix-dependent fractionation. In this work, MDC phlogopite (the source mineral for Mica-Mg nano-powder) was used as the secondary RM, consistently producing accurate Rb–Sr dates for a series of natural biotites and K-feldspars with well-characterized expected ages. However, biotite from the Banalasta Adamellite, Taratap Granodiorite and Entire Creek pegmatite are also suitable secondary RMs for Rb/Sr ratio calibration purposes with consistently <1.5% fully propagated uncertainties in our methodological approach. Until calibration using isochronous natural standards as the primary RM becomes possible in data-reduction software, the two-step calibration approach described here is recommended.

Keywords: reaction-cell ICP-MS; in-situ geochronology; Rb–Sr reference materials; calibration standards

1. Introduction

Rubidium-Strontium (Rb–Sr) geochronology using laser ablation – inductively coupled plasma – tandem mass spectrometry (LA-ICP-MS/MS) has become a popular method to constrain the formation or cooling age of potassium-bearing minerals (Gorojovsky and Alard, 2020; Hogmalm et al., 2017; Jegal et al., 2022; Kirkland et al., 2023; Larson et al., 2023; Laureijs et al., 2021; Li et al., 2020; Liebmann et al., 2022; Olierook et al., 2020; Redaa et al., 2021; Rosel and Zack, 2022; Sengun et al., 2019; Tillberg et al., 2021; Tillberg et al., 2020; Wang et al., 2022; Zack and Hogmalm, 2016). In contrast to traditional Rb–Sr dating involving column-chemistry in

https://doi.org/10.5194/egusphere-2023-1915
Preprint. Discussion started: 12 September 2023

specialized laboratories, the laser-ablation method allows rapid acquisition of Rb–Sr dates directly from thin sections or rock blocks with minimal sample preparation. The method involves the use of an ICP-MS/MS, equipped with a reaction cell where isobaric isotopes can be chemically separated due to their significant differences in reactivity with an introduced reaction gas (Balcaen et al., 2015 and references therein). Applied to Rb–Sr geochronology, CH_3F, SF_6, O_2 and N_2O have been used as reaction gasses (e.g. Hogmalm et al., 2017; Moens et al., 2001; Zack and Hogmalm, 2016), with the latter being the most widely used for quadrupole ICP-MS/MS due to its high reactivity. However, published analytical methodologies for LA-ICP-MS/MS Rb–Sr dating vary significantly beyond the applied reaction gas (Table 1). Reported laser conditions (fluence and repetition rate) are largely laser-wavelength dependent with common conditions being either ~5 - 7 J.cm^{-2} / 10 Hz for 213nm lasers, especially during initial development work (e.g. Hogmalm et al., 2017; Laureijs et al., 2021; Rosel and Zack, 2022; Sengun et al., 2019; Tillberg et al., 2020; Zack and Hogmalm, 2016) or ~2 - 4 J.cm^{-2} / 5 Hz for 193nm lasers (e.g. Kirkland et al., 2023; Larson et al., 2023; Li et al., 2020; Liebmann et al., 2022; Olierook et al., 2020; Redaa et al., 2021). The applied calibration protocols for mass discrimination and elemental fractionation, however, vary more significantly. Most published work uses a glass reference material (RM), with NIST-610 being most popular to correct for drift and calibrate the Sr isotopic ratios. Rb/Sr ratios are most commonly calibrated against Mica-Mg, a phlogopite prepared as a pressed nano-powder pellet, regardless of the analysed mineral (micas in most published work). However, the approach varies, with some methods directly calibrating to Mica-Mg as the primary RM (e.g. Gorojovsky and Alard, 2020; Hogmalm et al., 2017; Li et al., 2020; Redaa et al., 2021; Rosel and Zack, 2022; Sengun et al., 2019; Wang et al., 2022) and others using NIST-610 as the primary RM followed by a correction for matrix-dependent fractionation against Mica-Mg as

https://doi.org/10.5194/egusphere-2023-1915
Preprint. Discussion started: 12 September 2023

secondary RM (e.g. Liebmann et al., 2022; Olierook et al., 2020). Other secondary RMs, used to verify the accuracy of obtained dates, are either glass reference materials (e.g. Larson et al., 2023; Laureijs et al., 2021; Rosel and Zack, 2022) or in-house natural materials such as the La Posta biotite (Zack and Hogmalm, 2016), the MDC phlogopite (Redaa et al., 2021), or the CK001 biotite (Olierook et al., 2020).

In addition, laser-induced down-hole fractionation (DHF) can occur during ablation and aerosol condensation processes and is most apparent when ratioing elements with contrasting volatilities (e.g. Jackson and Günther, 2003; Košler et al., 2005; Longerich et al., 1996). Elemental Sr is more refractory than the volatile Rb and hence has a high potential to fractionate during laser ablation (Zack and Hogmalm, 2016). A small number of studies have directly compared different calibration approaches and have described differences in Rb–Sr DHF behaviour between commonly used reference materials (e.g. Redaa et al., 2021; Wang et al., 2022). However, systematic comparisons between data reduction protocols, tested with natural materials, are limited in the current literature. Here, we compare four different calibration approaches for a series of natural biotite and K-feldspar samples. The samples were taken from quickly cooled igneous rocks, eliminating potential diffusion-related issues when comparing dates of different minerals. Hence, the well-constrained igneous crystallization ages are the expected reference ages for the analysed samples and one of the biotite samples has previously been dated by the Rb–Sr ID-TIMS method. The calibration approaches we compare are:

(A) NIST-610 as the primary RM for both $^{87}Rb/^{87}Sr$ and $^{87}Sr/^{86}Sr$ ratios plus MDC phlogopite as secondary RM to correct for matrix-dependant fractionation;

(B) NIST-610 as the primary RM for both $^{87}Rb/^{87}Sr$ and $^{87}Sr/^{86}Sr$ ratios plus Mica-Mg pressed pellet as secondary RM to correct for matrix-dependant fractionation;

https://doi.org/10.5194/egusphere-2023-1915
Preprint. Discussion started: 12 September 2023

(C) Mica-Mg as the primary RM for $^{87}Rb/^{87}Sr$ ratios and NIST-610 as the primary RM for $^{87}Sr/^{86}Sr$ ratios;

(D) Mica-Mg as the primary RM for both $^{87}Rb/^{87}Sr$ and $^{87}Sr/^{86}Sr$ ratios

We discuss the differences between these approaches in terms of accuracy and precision, and highlight the importance of monitoring and correcting down-hole fractionation with appropriate reference materials.

2. Sample descriptions

2.1. MDC phlogopite and Mica-Mg nano powder

Mica-Mg nano-powder is used as a reference material for Rb–Sr dating. It consists of crushed phlogopite from Bekily (Madagascar) with a high Rb (1300 ± 40 µg.g^{-1}) and low Sr (27 ± 3 µg.g^{-1}) concentration (Redaa et al., 2023 and references therein). MDC is natural phlogopite, which was sourced from the same locality as Mica-Mg (Redaa et al., 2021). The reference age for both materials is 519.4 ± 6.5 Ma and the initial $^{87}Sr/^{86}Sr$ ratio is 0.72607 ± 0.0007, constrained from a diopside (low-Rb mineral) that occurs in the same location (Hogmalm et al., 2017). However, for Mica-Mg some pellet to pellet variation in both Rb/Sr and Sr/Sr ratios has been observed (Jegal et al., 2022; Redaa et al., 2023).

2.2. Entire Creek pegmatite

The Entire Creek sample was taken from a deformed pegmatite in the Harts Range meta-igneous complex of central Australia, in the same location as described by Mortimer et al. (1987). The pegmatite cross-cuts folded and foliated amphibolites, is composed of coarse-grained quartz,

https://doi.org/10.5194/egusphere-2023-1915
Preprint. Discussion started: 12 September 2023

plagioclase, alkali feldspar and biotite, with the latter defining a strong axial-plane foliation to folds outlined by the pegmatite. Biotite and whole-rock Rb/Sr and Sr/Sr isotope ratios, obtained by ID-TIMS at the University of Adelaide, are reported in Mortimer et al. (1987) and define a 7-point (3 biotite and 4 whole rock analyses) isochron age of 312.1 ± 1.8 / 5.1 Ma (95% confidence uncertainties, without / with overdispersion), recalculated in IsoplotR (Vermeesch, 2018), using the Villa et al. (2015) Rb–Sr decay constant of $1.3972 \pm 0.0045 \times 10^{-11}$ a^{-1} (Appendix 1).

2.3. Banalasta Adamellite (Bundarra Suite)

The S-type Banalasta Adamellite forms the southern end the Bundarra Batholith in the Southern New England Orogen in eastern Australia (e.g. Flood and Shaw, 1975; Jeon et al., 2012; Rosenbaum et al., 2012; Shaw and Flood, 1981). The Bundarra Batholith is an elongate north-south trending magmatic suite, spanning approximately 200 km. The Banalasta Adamellite is approximately 40 km in diameter and has sharp contacts with surrounding metasediments with a contact metamorphic aureole characterised by fine-grained cordierite-bearing assemblage at the pluton margin grading out to regional prehnite-pumpellyite metagreywacke assemblages over a distance of approximately 3 km (Flood and Shaw, 1977). Internally the granite is massive, coarse-grained granitoid containing approximately equal proportions of K-feldspar and plagioclase, together with accessory apatite, zircon and monazite. Biotite predominantly occurs in multi-grain clots together with quartz, plagioclase, magnetite, zircon and apatite. In rare cases they contain relic garnet, suggesting they formed from hydration of garnet entrained from the granitic source region.

Melt-precipitated zircon from the Banalasta Adamellite gives zircon U-Pb ages of 286.2 ± 2.2 Ma (Black, 2007), 289.2 ± 1.7 Ma (Jeon et al., 2012) and 282 ± 4 Ma (Phillips et al., 2011). Whole rock Rb–Sr data from the Bundarra Suite gives an age of 285 ± 15 Ma (n = 6/7, MSWD = 0.4).

https://doi.org/10.5194/egusphere-2023-1915
Preprint. Discussion started: 12 September 2023

When additional feldspar Rb–Sr data are included in the isochron, the isochron age is 283 ± 10 Ma (n = 9/10, MSWD = 0.24) (Appendix 2). Both isochron dates were recalculated using the data from Flood and Shaw (1977) and the decay constant from Villa et al. (2015). Additionally, Hensel et al (1995) reported a model whole rock Rb–Sr age of 287 ± 10 Ma for a group of 16 samples from the Bundarra Suite. Overall, it is evident that Rb–Sr age data is similar to the ages of melt precipitated zircon, consistent with the lack of evidence for extended fractional crystallisation (Jeon et al 2012). The samples used in this study come from the same location as Black (2007) that has a granitic zircon of 286.2 ± 2.2 Ma, as well as a second location approximately 800 meters away.

2.4. Taratap Granodiorite

The Taratap Granodiorite in the Delamerian Orogenic belt in southern Australia is classified as S-type, calc-alkaline with a composition dominated by microcline megacrysts (c. 3–4 cm in length), which define a NNE-trending magmatic fabric in a coarse-grained groundmass of plagioclase, quartz, K-feldspar and biotite, with accessory zircon, apatite, and monazite. Low-temperature alteration is evident in thin section by the presence of chlorite–muscovite–titanite and minor allanite (Burtt and Abbot, 1998). The sample was chosen for analysis because the timing of emplacement is tightly constrained by a zircon U-Pb ID-TIMS age of 497.11 ± 0.56 Ma ($^{206}Pb/^{238}U$ weighted mean age, 95% confidence interval uncertainty, MSWD = 1.8, n = 6) and an apatite Lu-Hf age of 497.1 ± 5.5 Ma (MSWD = 1.1, n = 38) (Glorie et al., 2023 and references therein).

3. Analytical methods

https://doi.org/10.5194/egusphere-2023-1915
Preprint. Discussion started: 12 September 2023

All Rb–Sr analyses were conducted at Adelaide Microscopy, University of Adelaide, using an Agilent 8900x ICP-MS/MS, coupled to a RESOlution-LR ArF excimer (193 nm) laser ablation system. A squid mixing device (Laurin Technic) was used to smooth the pulsed laser signal between the laser and the mass-spectrometer. The instrument parameters follow those reported in Redaa et al. (2021), with ablation in a He atmosphere (350 mL.min^{-1}), mixed with Ar (890 mL.min^{-1}) as the carrier gas and N_2 (3.5 mL.min^{-1}) added before the ICP torch to enhance the signal sensitivity. N_2O (0.37 mL.min^{-1}) was used as the reaction gas to separate ^{87}Sr from ^{87}Rb. The ^{86}Sr and ^{87}Sr isotopes were measured as their oxide reaction products (e.g. $^{87}Sr^{16}O$) with a mass shift of 16 amu between the two quadrupole mass analysers (e.g. Q1 = 87 m/z, Q2 = 103 m/z). Despite the high reaction efficiency of ^{87}Sr, residual unreacted Sr prevents direct measurement of ^{87}Rb. Instead, ^{85}Rb was measured as a proxy for ^{87}Rb and calculated assuming natural isotopic abundance. The samples and reference materials were ablated using a circular laser beam of 67 µm diameter, a fluence of 3.5 J.cm^{-2}, and repetition rate of 5 Hz. Further details are presented in Table 2. A total of three analytical sessions were conducted, with largely identical instrumental parameters between the different sessions. The ICP-MS was tuned to a sensitivity which kept Rb in pulse mode in Mica-Mg (the material with the highest Rb concentration), negating the requirement for additional pulse-analogue (P/A) corrections.

For each analytical session, NIST-610, Mica-Mg and MDC were used as reference materials for calibration purposes. All data was processed in LADR (Norris and Danyushevsky, 2018) using a customized data reduction algorithm that calculates error correlations from the raw isotopic ratios for each sweep in an analysis, in the same way as for U-Pb data reduction. Isotope ratios were calculated by: (1) correcting down-hole fractionation (DHF) against the primary RM, (2) averaging

https://doi.org/10.5194/egusphere-2023-1915
Preprint. Discussion started: 12 September 2023

the DHF corrected ratios of each sweep in the analysis, and then (3) normalising to a the primary RM to correct for matrix independent instrument mass bias and drift.

Normalisation of the measured Rb/Sr and Sr/Sr ratios was conducted with two different reference materials (NIST-610 and Mica-Mg), following the four analytical protocols outlined above (A-D). The reference $^{87}Rb/^{87}Sr$ and $^{86}Sr/^{87}Sr$ ratios used for Mica-Mg were 83.4 ± 1.0 and 0.53981 ± 0.00070, respectively (Hogmalm et al., 2017). For NIST-610, the $^{87}Rb/^{87}Sr$ was calculated from ppm data as 3.28 ± 0.03 and for the $^{86}Sr/^{87}Sr$ ratio, the reference value of 1.409048 ± 0.000036 was used (Woodhead and Hergt, 2001). For each normalization protocol, DHF corrections of the Rb–Sr ratios were applied based on the DHF behaviour of the applied primary RM. No DHF correction was applied to the $^{86}Sr/^{87}Sr$ ratios. Where NIST-610 was used as the primary RM, MDC phlogopite or Mica-Mg were used as secondary RM to correct the $^{87}Rb/^{87}Sr$ ratios for matrix-dependant fractionation (cfr. Roberts et al., 2017 for U/Pb ratios; Simpson et al., 2022 for Lu/Hf ratios).

All mica samples (including biotite samples and MDC phlogopite) were ablated with the laser ablating parallel to cleavage. The Bundarra samples were analysed in thin section and the Taratap sample as a rock block. The coarse Entire Creek biotites were mounted as mica-books using a vice to prevent air-gaps between individual mica sheets, with the ‘pages’ of the book mounted upright exposing multiple cleavage planes perpendicular to the surface.

For each sample and reference material, inverse isochron Rb–Sr dates (Li and Vermeesch, 2021) were calculated in IsoplotR (Vermeesch, 2018), based on the processed $^{87}Rb/^{87}Sr$ and $^{86}Sr/^{87}Sr$ ratios, their 2SE uncertainties, and the calculated error correlations. Reported inverse isochron uncertainties are fully propagated 95% confidence intervals, including the uncertainty on the decay constant and added uncertainty for overdispersion where required (calculated in IsoplotR). The

https://doi.org/10.5194/egusphere-2023-1915
Preprint. Discussion started: 12 September 2023

exceptions are the inverse isochron dates for MDC and Mica-Mg when used as secondary RMs, which are used to correct the Rb/Sr ratios when calibrating to NIST-610. For these cases the reported uncertainties are 95% confidence uncertainties without external uncertainties (as the external uncertainties would otherwise be applied twice to the isochron dates of the analysed samples). Session-dependant correction factors (CF) were calculated from the measured $^{87}Rb/^{87}Sr$ ratio for MDC and Mica-Mg and compared to the reference value (calculated from the published age for both MDC and Mica-Mg of 519.4 ± 6.5 Ma; Hogmalm et al., 2017; Redaa et al., 2021). These CF values (= measured ratio/expected ratio) were subsequently applied to each unknown analysis when calibrated to either MDC or Mica-Mg. Finally, the uncertainties on the MDC and Mica-Mg dates are propagated to the reported Rb–Sr isochron uncertainties for each NIST-610 calibrated sample using the quadratic addition of the relative uncertainties.

4. Results

4.1. Downhole fractionation trends

In this section, we compare the downhole fractionation (DHF) trend of the $^{87}Rb/^{87}Sr$ ratio between the analysed feldspars and micas and the reference materials (NIST-610 and Mica-Mg) (Fig. 1). The obtained fractionation trends do not vary significantly between different sessions; however, data from analytical session 3 is presented as it contains data for all analysed samples presented in this paper. The DHF trends were calculated in LADR and individual scatter plots can be found in Appendix 3. As shown, The DHF trends for the analysed biotite, phlogopite and K-feldspar samples are internally consistent, showing ~10% increase in Rb/Sr ratio over the first 20 s of ablation, followed by a flatter trend in the subsequent 20 s. NIST-610 shows a similar trend of increasing Rb/Sr ratio with ablation time, however the amplitude of the DHF curve is more

https://doi.org/10.5194/egusphere-2023-1915
Preprint. Discussion started: 12 September 2023

subdued compared to the natural samples (~3.5% increase in the first 20 s ablation). In contrast, the DHF pattern for Mica-Mg shows an oscillating trend, increasing for the first ~10 s of ablation and then dropping for the subsequent ~30 s of ablation (Fig. 1).

4.2. Within-session reproducibility of $^{87}Rb/^{87}Sr$ and $^{86}Sr/^{87}Sr$ ratios

Figure 2 shows the within-session variability of the $^{87}Rb/^{87}Sr$ and $^{86}Sr/^{87}Sr$ ratios for both primary RMs NIST-610 and Mica-Mg in analytical session 3. The reference materials are considered homogenous in both isotopic ratios, meaning that any variations are purely due to differences in the ablation characteristics from spot to spot. As shown, the measured $^{87}Rb/^{87}Sr$ ratios and $^{86}Sr/^{87}Sr$ ratios are significantly more consistent for NIST-610 compared to Mica-Mg (both measured using the same analytical conditions and spot size). The maximum within-session variability (=min-max range) in the $^{87}Rb/^{87}Sr$ ratio is < 3% for NIST-610, compared to > 8% for Mica-Mg. The $^{86}Sr/^{87}Sr$ ratio is more consistent for both primary RMs, however, the uncertainty on individual analyses is approximately 3× larger for Mica-Mg compared to NIST-610. ICP-MS mass-bias drift is minimal for both isotope ratios in NIST-610, with only a slight increase in the Rb/Sr ratio over the first 2-3 hours of analysis. As both Mica-Mg and NIST-610 were analysed sequentially in the same analytical session, the apparent 'drift' in the Mica-Mg $^{86}Sr/^{87}Sr$ ratios are due to variations in ablation rather than changes in the ICP-MS mass bias.

4.3. Isochron Rb–Sr dates for natural K-feldspars and micas

Inverse isochron plots and resulting Rb–Sr dates are presented for each analytical protocol in Appendix 4. Summary plots are shown in Figure 3. The data-table with the input $^{87}Rb/^{87}Sr$ and $^{86}Sr/^{87}Sr$ ratios is accessible from Figshare via the link in the data availability section. For the

https://doi.org/10.5194/egusphere-2023-1915
Preprint. Discussion started: 12 September 2023

Bundarra samples, the biotite isochrons are anchored to apatite Rb/Sr ratios, given that the apatites commonly occur as inclusions within biotite. For the K-feldspars, the isochrons are anchored to plagioclase, given that the analysed K-feldspars often show minor exsolution with plagioclase. However, the choice of anchoring mineral gives no difference in the obtained biotite and K-feldspar inverse isochron Rb/Sr dates. For the Taratap sample, isochron anchoring was conducted to a combination of plagioclase and apatite in session 1, but only plagioclase in sessions 2 and 3, given the limited occurrence of apatite in thin section. For the Entire Creek biotite sample, anchoring was conducted to whole-rock $^{86}Sr/^{87}Sr$ ratios from Mortimer et al. (1987). The MDC and Mica-Mg isochrons were anchored to an initial $^{86}Sr/^{87}Sr$ ratio of 1.3773 ± 0.0013 and calibrated to the published age of 519.4 ± 6.5 Ma (Hogmalm et al., 2017; Redaa et al., 2021).

The summary of obtained inverse Rb–Sr dates is presented in Table 3. As shown, there is only marginal variation in the absolute biotite dates between the three analytical protocols involving Mica-Mg, either as the primary RM for Rb/Sr ratios (protocols C & D) or as a secondary RM (protocol B). Hence, in order to evaluate the accuracy of the obtained Rb–Sr dates against the expected references ages for each sample, we only compare the first two analytical protocols (NIST-610 as the primary RM and either: (A) MDC or (B) Mica-Mg as secondary RM).

Figure 4 compares the obtained Rb–Sr inverse isochron dates to the expected ages for the three samples, that were analysed over two or three analytical sessions. The uncertainties for the K-feldspar dates are not shown as they are too large to be useful (due to the relatively low radiogenic nature of typical K-feldspar versus micas), here we only compare the accuracy of the absolute dates. As shown, analytical protocol (A) involving NIST as primary RM and MDC phlogopite as secondary RM consistently gives the most accurate Rb–Sr dates across all different analytical sessions. For this analytical protocol, the Rb–Sr biotite dates for the Bundarra samples are 287.1

https://doi.org/10.5194/egusphere-2023-1915
Preprint. Discussion started: 12 September 2023

268 ± 2.4 Ma, 284.7 ± 3.0 Ma, 287.7 ± 2.3 Ma and 285.7 ± 2.6 Ma (between two samples over two
269 analytical sessions), which are in excellent agreement with the published zircon U-Pb age of 286.2
270 ± 2.2 Ma (Black, 2007) from the same outcrop. The K-felspar dates of 290 ± 14 Ma, 285 ± 15 Ma,
271 290 ± 37 Ma and 288 ± 37 Ma are in excellent agreement as well but are less useful to evaluate
272 age accuracies given their larger uncertainties. Similarly for the Taratap sample, the obtained
273 biotite Rb–Sr dates of 499.4 ± 3.6 Ma and 495.7 ± 4.0 Ma as well as the (imprecise) K-feldspar
274 Rb–Sr dates of 500 ± 30 Ma, 501 ± 50 Ma and 495 ± 35 Ma are in excellent agreement with the
275 zircon U-Pb ID-TIMS age of 497.1 ± 0.6 Ma as well as the apatite Lu-Hf age of 497.1 ± 5.5 Ma
276 for the same sample (Glorie et al., 2023). Hence, the combined dataset suggests that the biotite, K-
277 feldspar and zircons record the same (crystallization) age for both the Bundarra and Taratap
278 samples. The Entire Creek biotite gave consistent Rb–Sr dates of 310.7 ± 1.5 Ma and 311.6 ± 3.1
279 Ma, in excellent agreement with the ID-TIMS age of 312.1 ± 1.8 / 5.1 Ma (95% confidence
280 uncertainties, without / with overdispersion), based on the Rb/Sr ratios in Mortimer et al. (1987),
281 recalculated with the Villa et al. (2015) Rb–Sr decay constant.

282 ## 5. Discussion

283 ### 5.1. Downhole fractionation corrections

284 Few previous studies have reported Rb–Sr DHF trends for a series of artificial reference materials
285 (i.e. glass standards and pressed pellets; Redaa et al., 2021; Wang et al., 2022). However, to the
286 best of our knowledge, DHF trends have not been evaluated for natural materials with the
287 exception of phlogopite MDC (Redaa et al., 2021). In our experiments, DHF is more pronounced
288 in natural micas and K-feldspar than observed for the NIST-610 glass and Mica-Mg pressed pellet,
289 when ablated under the same analytical conditions (Fig. 1). Comparatively, Mica-Mg appears least
290 appropriate to correct the analysed samples for DHF, given its systematically different DHF trend.

https://doi.org/10.5194/egusphere-2023-1915
Preprint. Discussion started: 12 September 2023

NIST-610 shows less DHF compared to the analysed micas and K-feldspars but its trend is more systematic (similar shape with lower amplitudes). Thus, correcting for DHF against NIST-610 reduces the observed DHF for the analysed samples, while Mica-Mg significantly under-corrects for DHF or accentuates it when applied to minerals. MDC biotite would be the most appropriate choice for DHF correction as it behaves very similar to the analysed mica and K-feldspar samples. However, as with most natural materials, MDC is not sufficiently homogenous in $^{87}Rb/^{87}Sr$ ratio to be used as a primary RM. While the shape or slope of DHF trends can vary depending on laser conditions (spot size, frequency and fluence), it cannot be eliminated for elements with contrasting volatilities such as Rb and Sr. However, based on the presented data, the use of NIST-610 is the more appropriate reference material to correct for DHF and Mica-Mg would exacerbate instead of reduce the effects of DHF.

If no DHF correction is applied, accurate data can only be achieved if exactly the same signal interval is selected in both the secondary RM and sample. If there is a residual DHF slope on the sample Rb/Sr ratios that is different to the RM (e.g. crystalline material versus Mica-Mg), then selecting a shorter signal interval can significantly bias Rb/Sr ratios and hence the apparent age.

5.2. Mica-Mg vs NIST-610 and MDC as calibration standards

5.2.1. Uncertainty comparisons

The contributions to the propagated uncertainties of individual analyses from the reference materials (average signal precision and calibration curve misfit) are much larger when calibrating to Mica-Mg compared to NIST-610 for both $^{87}Rb/^{87}Sr$ and $^{86}Sr/^{87}Sr$ ratios (Fig. 5). For example, in analytical session 1, the obtained uncertainties for individual $^{87}Rb/^{87}Sr$ ratios for the Entire Creek biotite sample are more than double when using Mica-Mg compared to NIST-610 as the

https://doi.org/10.5194/egusphere-2023-1915
Preprint. Discussion started: 12 September 2023

primary RM (Fig. 5; Appendix 5). As a result, the choice of Mica-Mg instead of NIST-610 as the primary RM might mask the presence of multiple data populations and introduces excessive uncertainties onto isochron dates.

The use of Mica-Mg as calibration standard for $^{86}Sr/^{87}Sr$ ratios most significantly affects the isochron precision of low-radiogenic samples such as K-feldspar samples. As shown in Table 3 and Figure 5, the uncertainty on the K-feldspar isochron dates can be up to 2× larger, compared to other calibration methods. Furthermore, the resulting MSWD values on the isochron regressions are consistently < 0.3 (Table 3), suggesting excessive uncertainties on individual data-points. For the more radiogenic biotite samples, the larger uncertainties in $^{86}Sr/^{87}Sr$ ratios have negligible effects to the precision on the isochron dates.

The precision of the calibrated $^{87}Rb/^{87}Sr$ ratios is more important to the isochron uncertainty of highly radiogenic materials, such as most types of micas. Calibrating to NIST-610 versus Mica-Mg yields either more precise biotite isochron dates or identical precision. However, when NIST-610 is used as the primary RM, propagation of the uncertainty on MDC or Mica-Mg to the resulting isochron age uncertainty is either identical or slightly worse compared to using Mica-Mg as calibration standard (Fig. 5; Table 3). The difference relates to the degree of overdispersion. The larger uncertainties on the Rb/Sr ratios when using Mica-Mg as primary RM result in lower MSWD values, reducing the uncertainty on the isochron regression. This excess uncertainty when calibrating to Mica-Mg might mask meaningful geological scatter in Rb/Sr ratios and it is therefore advisable to produce isochrons based on data with the best possible analytical precision.

In summary, Mica-Mg should not be used as calibration standard for $^{86}Sr/^{87}Sr$ ratio calculations for low-radiogenic samples as it introduces excessive uncertainties to age calculations. For high-radiogenic samples, using Mica-Mg as the primary RM also introduces larger uncertainties to

https://doi.org/10.5194/egusphere-2023-1915
Preprint. Discussion started: 12 September 2023

337 individual data-points compared to using NIST-610, but there is no significant difference in
338 propagated uncertainty after secondary correction to either MDC or Mica-Mg. For Rb/Sr ratio
339 calibrations, NIST-610 is more consistent, resulting in lower uncertainties on individual Rb/Sr
340 ratios. When there is no overdispersion, this results in better isochron age precision. However,
341 overdispersion can be masked by the increased uncertainties on Rb/Sr ratios, resulting in better
342 apparent precision when data is calibrated to Mica-Mg.

343 **5.2.2. Accuracy comparisons**

344 It has been observed previously that Rb–Sr dates are offset from their expected ages when
345 calibrated to the NIST-610 reference material (e.g. Gorojovsky and Alard, 2020; Wang et al.,
346 2022). In contrast, Mica-Mg seems to better reproduce expected ages, although the significant
347 uncertainties obtained for natural materials in previous studies render appropriate accuracy testing
348 difficult. For example, Wang et al. (2022) compares measured to expected Rb–Sr dates for three
349 samples with known ages. The best achieved uncertainty in their experiment was ~2.6% for one
350 sample, while for the other samples the reported uncertainties are ~5.6 and 6.3 %. Similarly, the
351 accuracy comparisons in Gorojovsky and Alard (2020) use the Monastery phlogopite, with a
352 precision of ~4% when calibrated to Mica-Mg. Both papers report data normalized to NIST-610
353 but do not apply a secondary correction for matrix-dependent fractionation.
354 For the biotites analysed in our study, the fully propagated 95% confidence interval uncertainties
355 ranges between 0.8 and 1.6% when calibrated to Mica-Mg and between 1.0% and 1.4% when
356 calibrated to NIST-610 and corrected to MDC (depending on the sample and analytical session;
357 Table 3), allowing for more detailed accuracy comparisons. Figure 4 illustrates that using NIST-
358 610 and MDC as calibration reference materials produces the most accurate results, compared to
359 the expected references dates. For the biotite results, the obtained Rb–Sr dates are within 0.5%

https://doi.org/10.5194/egusphere-2023-1915
Preprint. Discussion started: 12 September 2023

accuracy compared to the expected ages. The K-feldspar dates are accurate within 1%, except for session 2, where accuracy is within 1.5%. When the same data is calibrated against Mica-Mg (either using NIST-610 as the primary RM and Mica-Mg as secondary RM, or directly using Mica-Mg as the primary RM), the results are significantly offset from their expected ages. For the biotite results calibrated to Mica-Mg, accuracy is within 2% for sessions 2 and 3 and there is 5% age off-set in session 1. For the K-felspars, the age offset is up to 2.5% in sessions 2 and 3 and 6% in session 1. While the age offsets in sessions 2 and 3 might be regarded as `acceptable`, given the obtained precision, the more significant inaccuracy in session 1 renders Mica-Mg to be less desirable as a primary RM.

The difference in accuracy between session 1 and sessions 2 and 3 can be explained by the difference in measured dates for the MDC and Mica-Mg reference materials, normalised to NIST-610. For sessions 2 and 3, MDC and Mica-Mg produced similar isochron dates (2.3 and 1.9% difference respectively) (Table 3; Fig. 6). For session 1, however, MDC gives a significantly different age (494 ± 4 Ma) compared to Mica-Mg (469 ± 4 Ma). These differences in accuracy (ca. 5 % in session 1 and ca. 2 % in sessions 2 and 3) are in line with the observed age off-sets between the measured dates and reference dates for the biotite and K-feldspar samples, calibrated to Mica-Mg.

5.2.3. Long-term comparison between MDC and Mica-Mg as secondary calibration standards

Given that the accuracy of the Rb–Sr method appears to be significantly dependent on the applied calibration reference materials, and that the measured Rb–Sr dates of these calibration standards fluctuate significantly between analytical sessions when compared to NIST-610, the long-term

https://doi.org/10.5194/egusphere-2023-1915
Preprint. Discussion started: 12 September 2023

behaviour of the MDC and Mica-Mg reference materials needs to be evaluated. Figure 7 presents 2.5 years of measured Rb–Sr dates for MDC and Mica-Mg, both calibrated to NIST-610 as the primary RM. All data in this plot have been processed identically. The Rb–Sr dates for Mica-Mg are generally more consistent, ranging between ca. 462 and 479 Ma, with a standard deviation of 4.5 Ma, while the MDC dates show more variation, ranging between ca. 465 and 494 Ma, with a standard deviation of 7.7 Ma. In all but two sessions, MDC produces an older Rb–Sr date compared to Mica-Mg. The analytical sessions discussed above are highlighted in Figure F and encompass the maximum variability in measured Rb–Sr dates for MDC. With the premise that calibration to NIST-610 and MDC produces accurate Rb–Sr dates (as discussed in section 5.2.2), the difference between the measured MDC and Mica-Mg dates (Fig. 6, 7) can be regarded as an estimate of the degree of inaccuracy when data is calibrated to Mica-Mg. While some sessions reveal very little off-set between both standards, using Mica-Mg as calibration standard can lead to up to 5% inaccuracy in Rb–Sr dates. The cause of the observed variability is currently unknown, however, in the second-to-last session with a significantly older Mica-Mg date compared to MDC, the analysed samples might have received a lower effective laser fluence compared to other sessions as the glass between the laser beam and samples was not cleaned prior to analysis. The lower fluence could change the effective matrix bias between NIST-610, Mica-Mg and MDC, however, calibration of biotite against MDC produces accurate results as demonstrated in section 5.2.2. In contrast, although Mica-Mg produces more consistent Rb–Sr dates between analytical sessions, these dates are unreliable given the variable and unsystematic degree of inaccuracy between sessions.

6. Conclusions

https://doi.org/10.5194/egusphere-2023-1915
Preprint. Discussion started: 12 September 2023

406 Based on our observations, the use of Mica-Mg as calibration reference material is not
407 recommended, for the following reasons:
408 (1) The down-hole fractionation (DHF) trend for Mica-Mg is not comparable with the DHF
409 trends of natural bitote, phlogopite and K-feldspar (Fig. 1). Using Mica-Mg to correct DHF
410 would exacerbate instead of reduce DHF in those minerals;
411 (2) Given the relatively poor reproducibility of $^{87}Rb/^{87}Sr$ ratios and significant uncertainty on
412 individual $^{87}Sr/^{86}Sr$ measurements (Fig. 2), Mica-Mg as primary RM or secondary RM
413 introduces excess uncertainty that can be avoided using a more consistent primary RM such as
414 NIST-610;
415 (3) We demonstrated that calibrating to Mica-Mg may lead to up to 5% inaccuracy in Rb–Sr
416 age (Fig. 4, 6, 7) and that the degree of inaccuracy is unsystematically session-dependant.
417 We suggest a different approach, involving (1) calibration of the $^{87}Rb/^{87}Sr$ and $^{87}Sr/^{86}Sr$ ratios to a
418 primary reference material with high Rb and Sr concentrations and homogenous isotopic ratios
419 such as NIST-610 glass, including DHF correction of the Rb/Sr ratios, followed by (2) a correction
420 of the $^{87}Rb/^{87}Sr$ ratio to a natural mineral secondary RM with a similar DHF trend as the samples
421 to be analysed. In our observations, there are no significant differences in matrix effects comparing
422 biotite, phlogopite and K-feldspar, suggesting that any of these natural minerals as secondary RM
423 can produce accurate dates for K-rich minerals. We have used MDC phlogopite as secondary RM
424 and demonstrate accurate Rb–Sr dates for a range of biotites and K-feldspars with well-established
425 age constraints. The fully propagated uncertainties for the analysed biotites are <1.5%, allowing
426 accuracy verifications at high analytical precision.

https://doi.org/10.5194/egusphere-2023-1915
Preprint. Discussion started: 12 September 2023

Finally, while this two-step calibration protocol is currently recommended due to current constraints with data processing software, new developments involving calibrating to isochronous reference materials might become the desired approach in the future.

Data availability

The Rb–Sr dataset used in this manuscript is freely available on figshare at https://doi.org/10.25909/23996484.

Acknowledgements

This paper was supported by research grant FT210100906 and DP220103037 from the Australian Research Council (ARC).

Author contributions

SG: Conceptualization, investigation, writing – original draft, methodology, funding acquisition, visualisation, formal analysis

SEG: Conceptualization, investigation, writing – review and editing, methodology

MH: Conceptualization, investigation, writing - review and editing, resources

JCL: Conceptualization, investigation, writing - review and editing, formal analysis

Competing interests

The authors declare that they have no conflict of interest.

Ethical statement

This manuscript is an original work that is not submitted or published elsewhere.

https://doi.org/10.5194/egusphere-2023-1915
Preprint. Discussion started: 12 September 2023

454 **Tables**

	React. gas ($ml.min^{-1}$)	Laser wavel. (nm)	Fluence ($J.cm^{-2}$)	Rep. rate (Hz)	Spot (µm)	Rb-Sr calibration	Sr-Sr calibration	DHF	Err. corr.
Zack and Hogmalm 2016	O_2 (0.25)	213	7	10	80	Pl: NIST 610; Ksp: BCR-2G; Bt: La Posta	NIST 610	No	No
Hogmalm et al. 2017	O_2 (0.25) N_2O (0.16) SF_6 (0.04)	213	O_2: 7 N_2O: 6-8 SF_6: 6-8	10 4-5 10	80 50 50	Mica-Mg	NIST 610	No	No
Tillberg et al. 2020	N_2O (?)	213	?	?	50	BCR-2G (Sec: Mica-Mg/La Posta)	NIST 610	No	Yes
Rösel and Zack 2022	N_2O (0.18-0.20)	213	5-7	10	50-60	Mica-Mg (sec: NIST 610 / BCR-2G)	Mica-Mg	No	No
Gorojovsky and Alard 2020	N_2O (0.25)	193 and 213	7.8	5	85	Mica-Mg	Mica-Mg, NIST 610, BHVO-2G	No	No?
Larson et al 2023	N_2O (0.37)	193	4	10	50	Mica-Mg (Sec: Mica-Fe)	NIST 610	Yes?	Yes
Laureijs et al. 2021	CH_3F (10%)	213	6	10	50	ATHO-G, T1-G, StHs6/80-G	NIST 612	No	Yes
Li et al. 2020	N_2O (0.35)	193	3.5	5	74	Mica-Mg Sec: MDC	Mica-Mg	No	No
Liebmann et al. 2022	N_2O (?)	193	2.5	5	64	NIST-610 + Mica-Mg Sec: CK001 bt	NIST-610	No	Yes (est)
Olierook et al. 2020	N_2O (0.25)	193	2.5	5	64-87	NIST-610 + Mica-Mg Sec: CK001 bt	NIST-610	No	No
Redaa et al. 2021	N_2O (0.37)	193	3.5	5	74	Mica-Mg Sec: MDC	Mica-Mg	monitored	No
Sengun et al. 2019	N_2O (?)	213	5.7	10	50	Mica-Mg	NIST 610	No	No
Tilberg et al. 2021	N_2O (?)	213	?	?	50	Mica-Mg / NIST 610	NIST 610	No	Yes
Wang et al. 2022	N_2O (0.25)	193	7	5	85	Mica-Mg	NIST 610, BHVO-2G, BCR-2G	monitored	No
Kirkland et al. 2023	N_2O (0.25)	193	2	5	64	Mica-Mg Sec: CK001 bt	NIST 610	No	No

https://doi.org/10.5194/egusphere-2023-1915
Preprint. Discussion started: 12 September 2023

455 **Table 1:** Summary of published analytical conditions and protocols for LA-ICP-MS/MS Rb–Sr
456 dating. Rep. rate = laser repetition rate; Sec = secondary reference material; Bt = biotite; ksp = K-
457 feldspar; Pl = plagioclase; Err. Corr. = error correlation calculated; est = estimated formula. In case
458 of method development work - `best conditions` are quoted.

459

https://doi.org/10.5194/egusphere-2023-1915
Preprint. Discussion started: 12 September 2023

Analytical conditions	
Plasma Settings	
RF power	1350 W
Sample Depth	5.0 mm
Ar carrier gas	0.89 L/min
He carrier gas	0.38 L/min
N_2 addition	4 mL/min
Lens Parameters	
Extract 1	1.5 V
Extract 2	-80 V
Omega Bias	-85 V
Omega Lens	5.0 V
Q1 entrance	-10 V
Q1 exit	-2.0 V
Cell focus	-2.0 V
Cell Entrance	-90 V
Cell Exit	-120 V
Deflect	10 V
Plate Bias	-80 V
Q1 bias	-2.0 V
Q1 Prefilter Bias	-10.0 V
Q1 Postfilter Bias	-10.0 V
N_2O gas flow	0.37 mL/min
Octopole bias	-6.0 V
Axial Acceleration	2.0 V
Octopole RF	180 V
Energy Discrimination	-7.0 V
Analysis Parameters	
Laser Wavelength	193 nm
Laser fluence	3.5 J/m2
Sample laser diameter	67 µm
Laser repetition rate	5 Hz
Background	30 s
Analysis time	40 s
Isotopes measured & dwell times (ms)	^{23}Na (2), ^{24}Mg (2), ^{27}Al (2), $^{29+16}$Si (2), $^{31+16}$P (2), ^{39}K (2), $^{43+16}$Ca (2), ^{55}Mn (2), $^{56+16}$Fe (2), ^{85}Rb (10), $^{86+16}$Sr (50), $^{87+16}$Sr (50), $^{88+16}$Sr (50), $^{89+16}$Y (5), $^{90+32}$Zr (5), $^{93+32}$Nb (5), all $^{x+16}$REE (5), $^{232+15}$Th (5), $^{238+16}$U (5)

Table 2: Analytical conditions for the three LA-ICP-MS/MS sessions in this paper.

			(A) NIST + MDC		(B) NIST + Mica-Mg		(C) Mica-Mg & NIST		(D) Mica-Mg	
Sample (exp. age)	S	n	Age (± 2σ) [Ma]	MS WD	Age (± 2σ) [Ma]	MS WD	Age (± 2σ) [Ma]	MS WD	Age (± 2σ) [Ma]	MS WD
Ent Crk Bt	1	24	310.7 ± 1.5/2.5/3.1	1.1	327.8 ± 1.7/2.7/3.2	0.96	327.6 ± 3.3/3.9	0.27	328.8 ± 3.4/4.0	0.25
(312.1 ± 1.8[1])	3	20	311.6 ± 3.1/3.8/4.5	2.5	317.6 ± 3.2/3.8/4.6	2.4	316.1 ± 3.2/3.8	0.85	316.2 ± 3.2/3.8	0.84
Bund1b Bt	2	44	287.1 ± 1.6/2.4/3.4	1.6	280.3 ± 1.5/2.4/3.2	1.7	280.1 ± 1.6/2.4	0.97	280.2 ± 1.6/2.4	0.82
(286.2 ± 2.2[2])	3	22	284.7 ± 2.4/3.0/3.8	1.0	290.1 ± 2.5/3.1/3.8	1.1	288.4 ± 4.1/4.5	0.7	288.2 ± 4.3/4.7	0.28
Bund1b Ksp	2	57	290 ± 14/14/14	0.87	284 ± 14/14/14	0.88	284 ± 14/14	0.84	280 ± 23/23	0.3
(286.2 ± 2.2[2])	3	53	287 ± 15/15/15	0.88	292 ± 15/15/15	0.88	290 ± 15/16	0.86	283.4 ± 38/38	0.19
Bund6a Bt	2	38	287.7 ± 1.3/2.3/3.4	1.4	280.9 ± 1.3/2.2/3.1	1.5	279.5 ± 1.5/2.3	0.71	279.5 ± 1.5/2.3	0.7
(286.2 ± 2.2[2])	3	22	285.7 ± 1.9/2.6/3.4	0.74	291.2 ± 1.9/2.7/3.6	0.72	288.7 ± 3.5/4.0	0.54	288.8 ± 3.6/4.0	0.34
Bund6a Ksp	2	45	290 ± 37/37/37	0.69	283 ± 36/36/36	0.69	281 ± 36/36	0.68	283 ± 75/75	0.16
(286.2 ± 2.2[2])	3	40	288 ± 37/37/37	0.65	293 ± 38/38/38	0.65	294 ± 39/39	0.65	296 ± 93/93	0.11
Taratap Bt	2	30	499.4 ± 1.8/3.6/5.6	1.2	487.7 ± 1.7/3.5/5.2	1.2	489.6 ± 2.8/4.2	0.67	489.6 ± 2.8/4.2	0.63
(497.1 ± 0.6[3])	3	16	495.7 ± 2.5/4.0/5.5	1.2	505.1 ± 2.6/4.1/5.8	1.2	504.0 ± 5.4/6.3	0.51	504.0 ± 5.5/6.3	0.52
Taratap Ksp	1	54	500 ± 30/30/30	0.53	527 ± 31/31/31	0.53	527 ± 32/32	0.50	539 ± 58/58	0.14
(497.1 ± 0.6[3])	2	20	501 ± 50/50/50	0.58	490 ± 49/49/49	0.58	492 ± 50/50	0.56	494 ± 106/106	0.12
	3	18	495 ± 35/35/35	0.95	504 ± 36/36/36	0.95	490 ± 39/39	1.1	511 ± 63	0.3

463

464

			NIST-610 as primary RM	
Secondary RM	S	n	Age (± 2σ) [Ma]	MS WD
MDC	1	34	494.4 ± 3.0	1.4
	2	21	464.5 ± 4.0	1.3
	3	30	470.6 ± 3.6	1.1
MicaMG	1	35	468.6 ± 2.5	2.8
	2	21	475.7 ± 3.7	3.5
	3	20	461.8 ± 3.7	2.7

465

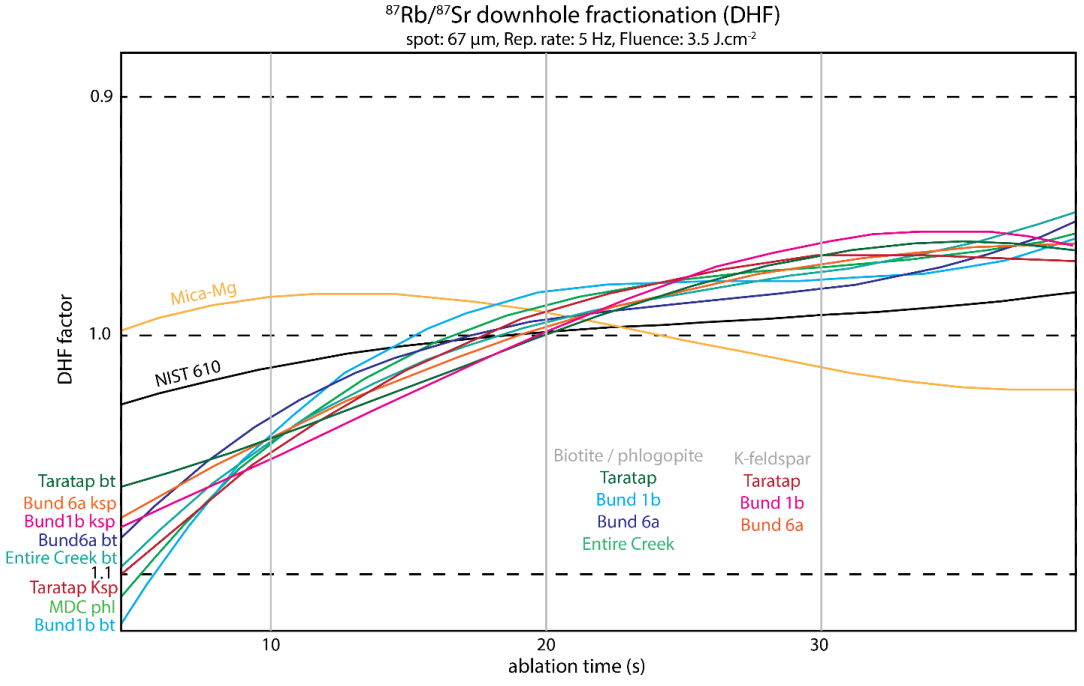
466

Table 3: Summary table of Rb–Sr dates obtained in this study. S = session number, n = number of analysed grains, exp. age = expected reference age (see below). All uncertainties are 95% confidence intervals and are reported as (1) excluding external uncertainty (on the decay constant) / (2) including external uncertainties / (3) with propagated uncertainty from the correction standard (for methods (A) and (B) only). (A) NIST-610 as primary RM and MDC as secondary RM to calibrate Rb/Sr ratios; (B) NIST-610 as primary RM, Mica-MG as secondary RM to calibrate Rb/Sr ratios; (C) Rb/Sr ratios calibrated to Mica-MG as primary RM and Sr/Sr ratios calibrated to NIST-610 as secondary RM; (D) Mica-MG as primary RM for both Rb/Sr and Sr/Sr ratios. [1] Rb-Sr TIMS age from Mortimer et al. (1987), recalculated with Villa et al. (2015) decay constant in IsoplotR (Vermeesch, 2018). The reported uncertainty is 95% confidence interval but does not take overdispersion into account. [2] Zircon U-Pb age for the Banalasta Adamellite in the Bundarra Suite, from Black (2007). [3] Zircon U-Pb TIMS age for the Taratap Granodiorite, reported in Glorie et al. (2023).

https://doi.org/10.5194/egusphere-2023-1915
Preprint. Discussion started: 12 September 2023

477 **Figure Captions**

478



479

480 **Figure 1:** $^{87}Rb/^{87}Sr$ downhole fractionation profiles for the analysed reference materials Mica-Mg
481 (yellow line) and NIST-610 (black line), the biotite / phlogopite (green-blue lines) and K-felspar
482 (red-pink lines) samples in analytical session 3, calculated in LADR (Norris and Danyushevsky,
483 2018). The DHF factor is calculated relative to the average ratio of the ablation signal (i.e. DHF
484 factor of 1 = average $^{87}Rb/^{87}Sr$ ratio of the downhole signal).

485

https://doi.org/10.5194/egusphere-2023-1915
Preprint. Discussion started: 12 September 2023

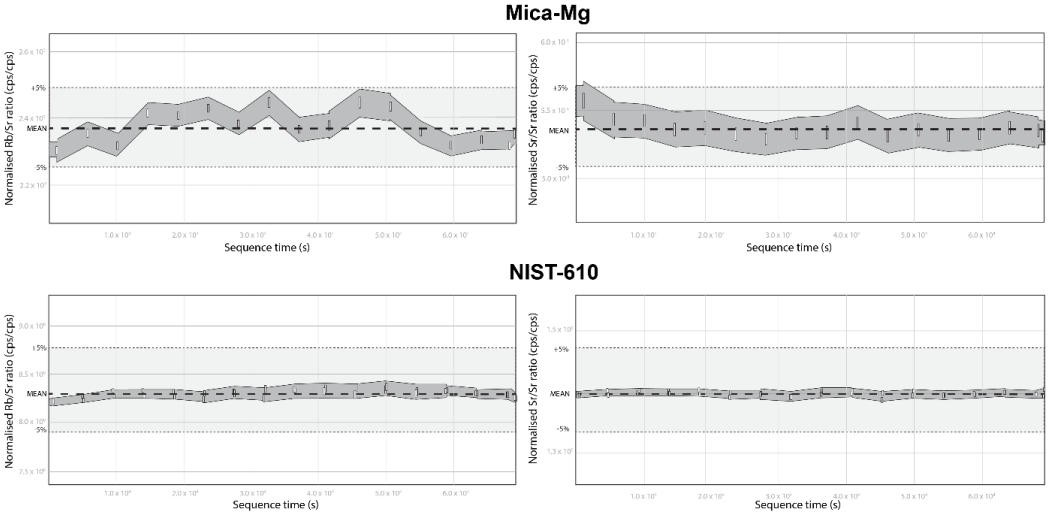


Figure 2: Variability of the $^{87}Rb/^{87}Sr$ and $^{86}Sr/^{87}Sr$ ratios for the analysed reference materials NIST-610 and Mica-Mg over the total duration of analytical session 3. All plots are scaled equally to ± 5% variation of the mean to aid visual comparisons. The vertical bars are ±1 standard deviation. The gray envelopes models ±2 standard deviation (note that for NIST-610 each standard was measured twice at each standard bracket).

https://doi.org/10.5194/egusphere-2023-1915
Preprint. Discussion started: 12 September 2023

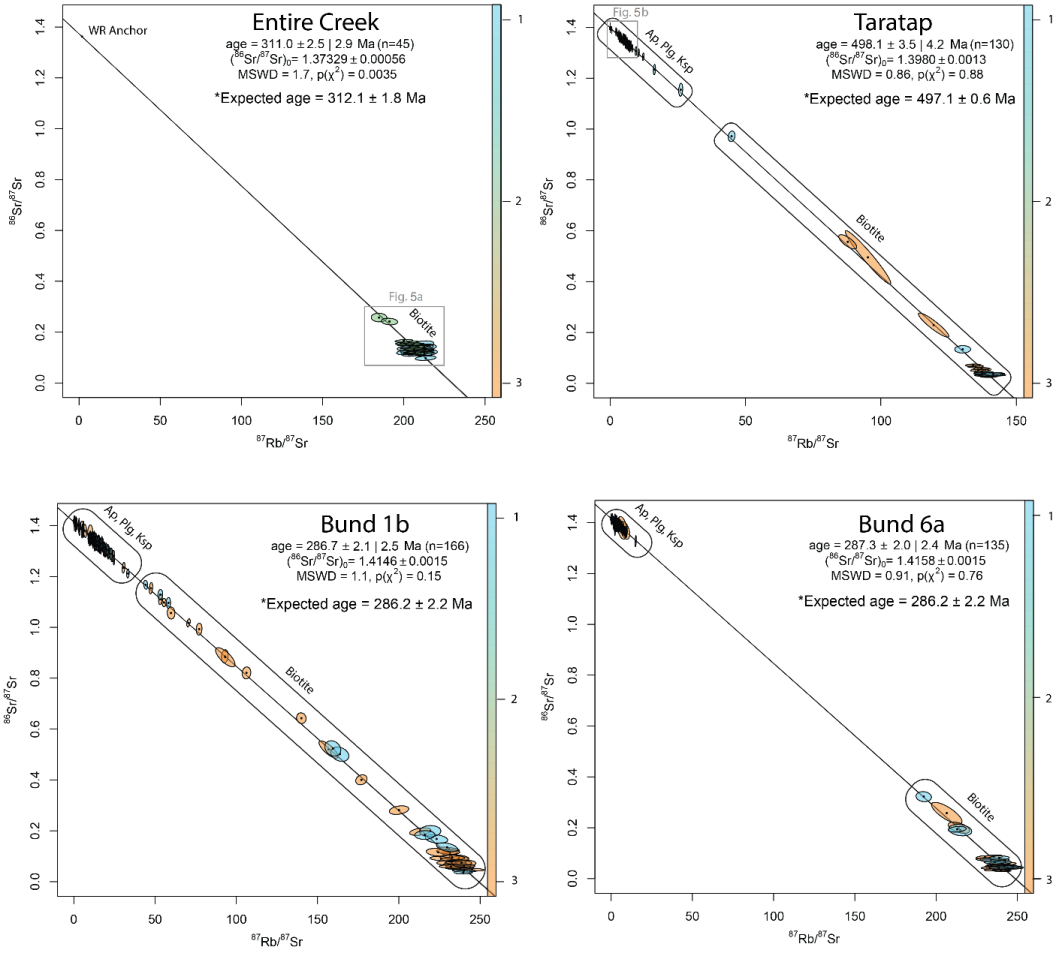
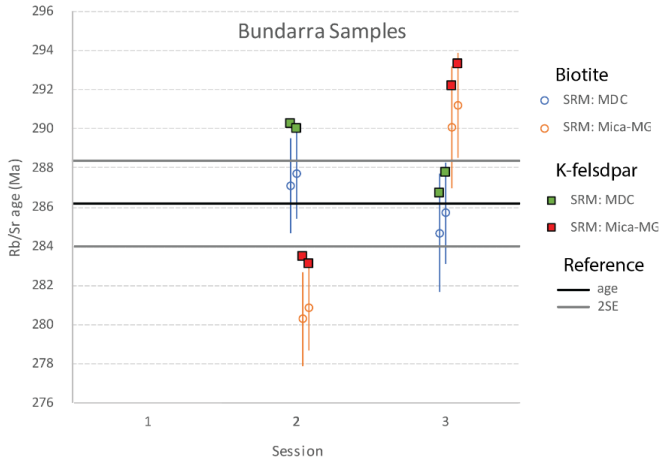


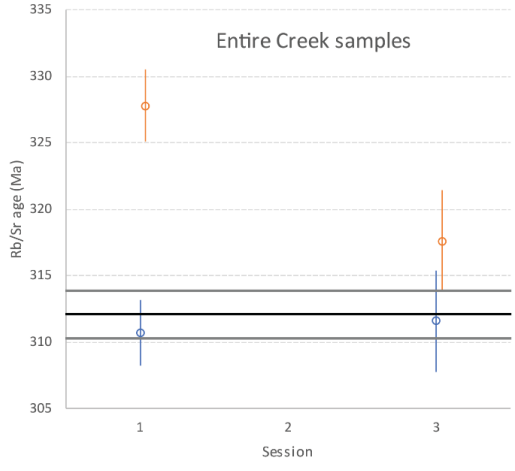
Figure 3: Pooled multi-mineral Rb–Sr isochron dates for the Entire Creek, Taratap and the two Bundarra samples (Bund 1b and Bund 6a). The data was calibrated against NIST-610 as primary RM and MDC as secondary RM (see text for details). The colour-code refers to the analytical session in which the data was obtained. Biotite analyses plot towards the radiogenic lower-intercept of the inverse isochrons, while feldspar and apatite anchor Rb/Sr ratios plot towards the low-radiogenic end of the isochron regression. All plots were calculated in IsoplotR (Vermeesch, 2018), reporting 95% confidence interval uncertainties (including the uncertainty on the decay-constant) with and without propagated uncertainty from the MDC secondary RM. Expected ages

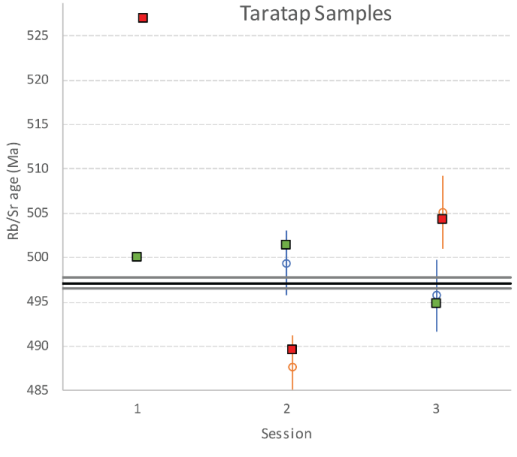
https://doi.org/10.5194/egusphere-2023-1915
Preprint. Discussion started: 12 September 2023

are the recalculated Rb–Sr age from Mortimer et al. (1987) with the Villa et al. (2015) decay constant for the Entire Creek sample; the zircon U-Pb ID-TIMS age reported in Glorie et al. (2023) for the Taratap sample, and the Zircon SHRIMP U-Pb age from Black (2007) for the Bundarra samples (see text for further details).

https://doi.org/10.5194/egusphere-2023-1915
Preprint. Discussion started: 12 September 2023







507

https://doi.org/10.5194/egusphere-2023-1915
Preprint. Discussion started: 12 September 2023

Figure 4: Comparisons of Rb–Sr dates over three analytical sessions, calibrated to either MDC or Mica-Mg as secondary RM, with respect to the expected ages for each sample (black line with gray 2SE uncertainty bars). In all cases, NIST-610 was used as primary RM. Biotite data are plotted as open circles (blue = calibrated to MDC as secondary RM, orange = calibrated to Mica-Mg as secondary RM). K-feldspar data are plotted as filled squares (green = calibrated to MDC as secondary RM, red = calibrated to Mica-Mg as secondary RM).

https://doi.org/10.5194/egusphere-2023-1915
Preprint. Discussion started: 12 September 2023

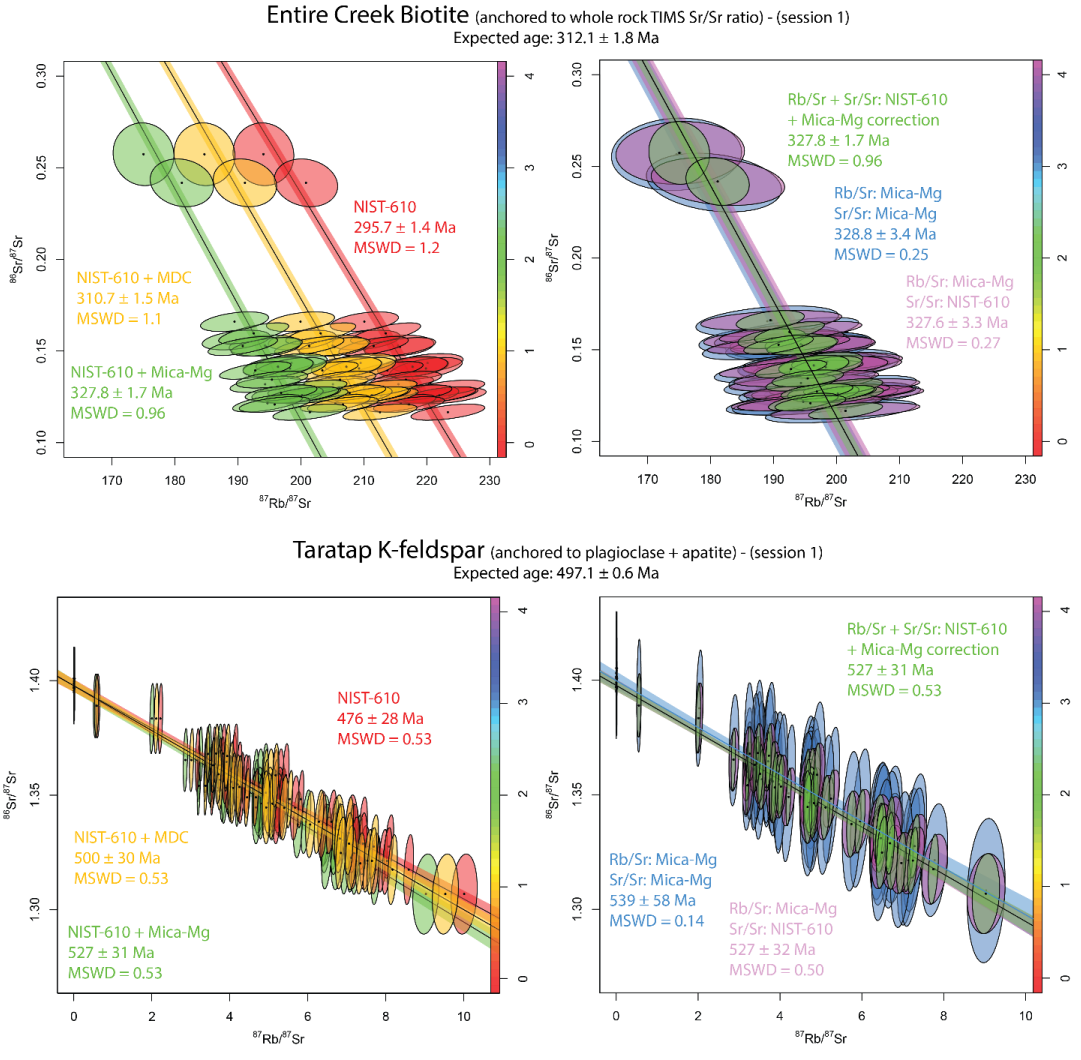


Figure 5: Comparisons of isochron dates obtained using the 4 different calibration protocols using the session 1 biotite Rb–Sr data from the Entire Creek sample and K-feldspar Rb–Sr data from the Taratap sample. Data plotted in red = NIST-610 as primary RM without correction for matrix-induced fractionation. Data plotted in green = NIST-610 as primary RM with Mica-Mg as secondary RM. Data plotted in yellow = NIST-610 as primary RM with MDC as secondary RM. Data plotted in purple = NIST-610 as primary RM for Sr/Sr ratios and Mica-Mg as primary RM

https://doi.org/10.5194/egusphere-2023-1915
Preprint. Discussion started: 12 September 2023

for Rb/Sr ratios. Data plotted in blue = both Rb/Sr and Sr/Sr ratios calibrated to Mica-Mg as primary RM. The biotite data are highly radiogenic and show significant age differences depending on the used secondary RM. The K-feldspar data are low radiogenic, resulting in larger and overlapping uncertainties (refer to Figure 3 for full isochron plots). Using NIST-610 as primary RM produces the smallest uncertainties on individual data-points.

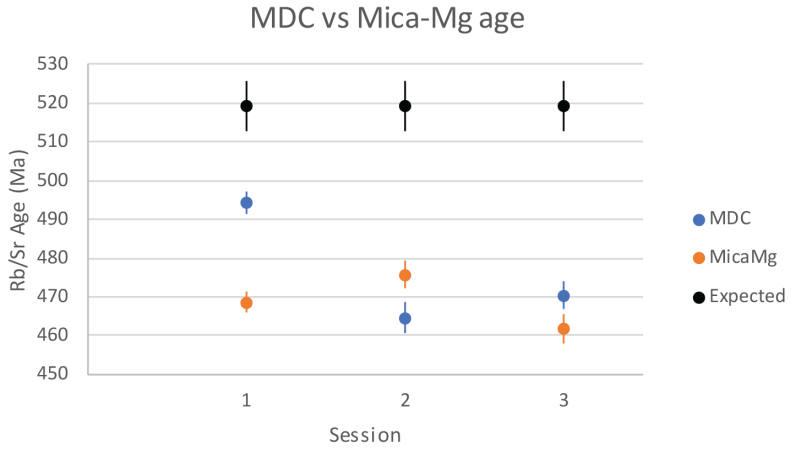


Figure 6: Rb–Sr dates for MDC and Mica-Mg calibrated to NIST-610 over the three analytical sessions used in this paper. The off-set of the Rb–Sr age with respect to the reference age is used to calculate the correction factor on the Rb/Sr ratios.

https://doi.org/10.5194/egusphere-2023-1915
Preprint. Discussion started: 12 September 2023

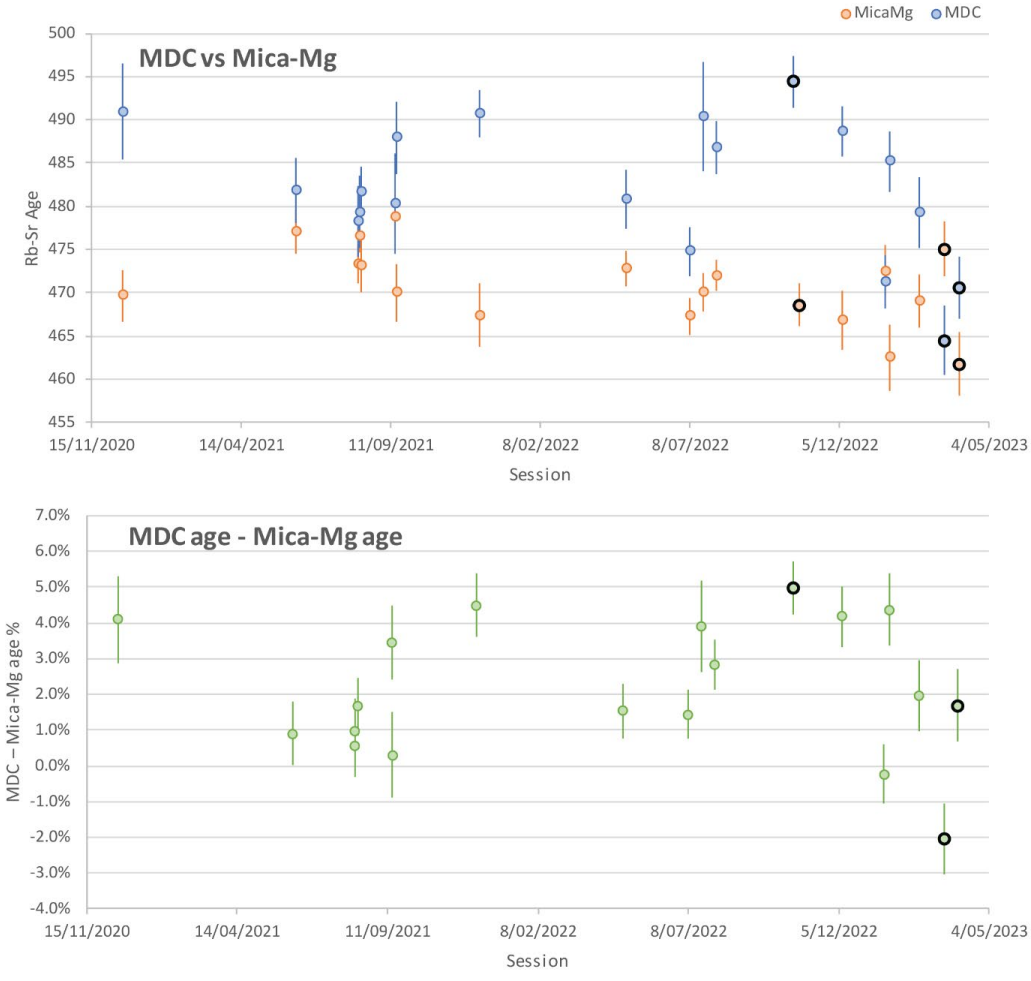


Figure 7: Long-term (2.5 years) Rb–Sr age data for Mica-Mg and MDC for the lab (Adelaide Microscopy). The top plot shows absolute dates and the bottom plot shows the percentage difference between the MDC and Mica-Mg dates. All data were processed in the same way using NIST-610 as primary RM. The three analytical sessions previously discussed are highlighted by black rims and capture the most extreme differences obtained in our lab to date. Given that MDC as secondary RM produces consistently accurate data, the plot indicates that Mica-Mg as primary RM can lead to up to 5% inaccuracy in Rb–Sr age calculations.

https://doi.org/10.5194/egusphere-2023-1915
Preprint. Discussion started: 12 September 2023

References

Balcaen, L., Bolea-Fernandez, E., Resano, M., Vanhaecke, F., 2015. Inductively coupled plasma – Tandem mass spectrometry (ICP-MS/MS): A powerful and universal tool for the interference-free determination of (ultra)trace elements – A tutorial review. Analytica Chimica Acta, 894: 7-19.

Black, L., 2007. SHRIMP U–Pb zircon ages obtained during 2006/07 for NSW Geological Survey projects.

Burtt, A.C., Abbot, P.J., 1998. The Taratap Granodioritite, South-East South Australia. MESA Journal, 10: 35-39.

Flood, R.H., Shaw, S.E., 1975. A cordierite-bearing granite suite from the New England Batholith, N.S.W., Australia. Contributions to Mineralogy and Petrology, 52(3): 157-164.

Flood, R.H., Shaw, S.E., 1977. Two "S-type" granite suites with low initial 87Sr/86Sr ratios from the New England Batholith, Australia. Contributions to Mineralogy and Petrology, 61(2): 163-173.

Glorie, S. et al., 2023. Robust laser ablation Lu-Hf dating of apatite: an empirical evaluation. Geological Society of London Special Publication, In press.

Gorojovsky, L., Alard, O., 2020. Optimisation of laser and mass spectrometer parameters for thein situanalysis of Rb/Sr ratios by LA-ICP-MS/MS. JOURNAL OF ANALYTICAL ATOMIC SPECTROMETRY, 35(10): 2322-2336.

Hogmalm, K.J., Zack, T., Karlsson, A.K.O., Sjoqvist, A.S.L., Garbe-Schonberg, D., 2017. In situ Rb-Sr and K-Ca dating by LA-ICP-MS/MS: an evaluation of N2O and SF6 as reaction gases. Journal of Analytical Atomic Spectrometry, 32(2): 305-313.

Jackson, S.E., Günther, D., 2003. The nature and sources of laser induced isotopic fractionation in laser ablation-multicollector-inductively coupled plasma-mass spectrometry. Journal of Analytical Atomic Spectrometry, 18(3): 205-212.

Jegal, Y. et al., 2022. Characterisation of Reference Materials for In Situ Rb-Sr Dating by LA-ICP-MS/MS. Geostandards and Geoanalytical Research, 46(4): 645-671.

Jeon, H., Williams, I.S., Chappell, B.W., 2012. Magma to mud to magma: Rapid crustal recycling by Permian granite magmatism near the eastern Gondwana margin. Earth and Planetary Science Letters, 319-320: 104-117.

Kirkland, C.L. et al., 2023. Dating mylonitic overprinting of ancient rocks. Communications Earth & Environment, 4(1): 47.

Košler, J. et al., 2005. Chemical and phase composition of particles produced by laser ablation of silicate glass and zircon—implications for elemental fractionation during ICP-MS analysis. Journal of Analytical Atomic Spectrometry, 20(5): 402-409.

Larson, K.P., Button, M., Shrestha, S., Camacho, A., 2023. A comparison of 87Rb/87Sr and 40Ar/39Ar dates: Evaluating the problem of excess 40Ar in Himalayan mica. Earth and Planetary Science Letters, 609: 118058.

Laureijs, C.T., Coogan, L.A., Spence, J., 2021. In-situ Rb-Sr dating of celadonite from altered upper oceanic crust using laser ablation ICP-MS/MS. Chemical Geology, 579.

Li, S.-S. et al., 2020. Coupled U-Pb and Rb-Sr laser ablation geochronology trace Archean to Proterozoic crustal evolution in the Dharwar Craton, India. Precambrian Research, 343: 105709.

Li, Y., Vermeesch, P., 2021. Short communication: Inverse isochron regression for Re–Os, K–Ca and other chronometers. Geochronology, 3(2): 415-420.

Liebmann, J., Kirkland, C.L., Kelsey, D.E., Korhonen, F.J., Rankenburg, K., 2022. Lithological fabric as a proxy for Rb-Sr isotopic complexity. Chemical Geology, 608.

https://doi.org/10.5194/egusphere-2023-1915
Preprint. Discussion started: 12 September 2023

Longerich, H.P., Günther, D., Jackson, S.E., 1996. Elemental fractionation in laser ablation inductively coupled plasma mass spectrometry. Fresenius' Journal of Analytical Chemistry, 355(5): 538-542.

Moens, L.J., Vanhaecke, F.F., Bandura, D.R., Baranov, V.I., Tanner, S.D., 2001. Elimination of isobaric interferences in ICP-MS, using ion–molecule reaction chemistry: Rb/Sr age determination of magmatic rocks, a case study. Journal of Analytical Atomic Spectrometry, 16(9): 991-994.

Mortimer, G.E., Cooper, J.A., James, P.R., 1987. U Pb and Rb Sr geochronology and geological evolution of the Harts Range ruby mine area of the Arunta Inlier, central Australia. Lithos, 20(6): 445-467.

Norris, A., Danyushevsky, L., 2018. Towards Estimating the Complete Uncertainty Budget of Quantified Results Measured By LA-ICP-MS. Goldschmidt, Boston, USA (2018).

Olierook, H.K.H. et al., 2020. Resolving multiple geological events using in situ Rb–Sr geochronology: implications for metallogenesis at Tropicana, Western Australia. Geochronology, 2(2): 283-303.

Phillips, G., Landenberger, B., Belousova, E.A., 2011. Building the New England Batholith, eastern Australia—Linking granite petrogenesis with geodynamic setting using Hf isotopes in zircon. Lithos, 122(1): 1-12.

Redaa, A. et al., 2023. Testing Nano-Powder and Fused-Glass Mineral Reference Materials for In Situ Rb-Sr Dating of Glauconite, Phlogopite, Biotite and Feldspar via LA-ICP-MS/MS. Geostandards and Geoanalytical Research, 47(1): 23-48.

Redaa, A. et al., 2021. Assessment of elemental fractionation and matrix effects during in situ Rb-Sr dating of phlogopite by LA-ICP-MS/MS: implications for the accuracy and precision of mineral ages. Journal of Analytical Atomic Spectrometry, 36(2): 322-344.

Roberts, N.M.W. et al., 2017. A calcite reference material for LA-ICP-MS U-Pb geochronology. Geochemistry, Geophysics, Geosystems, 18(7): 2807-2814.

Rosel, D., Zack, T., 2022. LA-ICP-MS/MS Single-Spot Rb-Sr Dating. Geostandards and Geoanalytical Research, 46(2): 143-168.

Rosenbaum, G., Li, P., Rubatto, D., 2012. The contorted New England Orogen (eastern Australia): New evidence from U-Pb geochronology of early Permian granitoids. Tectonics, 31(1).

Sengun, F., Erlandsson, V.B., Hogmalm, J., Zack, T., 2019. In situ Rb-Sr dating of K-bearing minerals from the orogenic Akcaabat gold deposit in the Menderes Massif, Western Anatolia, Turkey. JOURNAL OF ASIAN EARTH SCIENCES, 185.

Shaw, S.E., Flood, R.H., 1981. The New England Batholith, eastern Australia: Geochemical variations in time and space. Journal of Geophysical Research: Solid Earth, 86(B11): 10530-10544.

Simpson, A. et al., 2022. In situ Lu–Hf geochronology of calcite. Geochronology, 4(1): 353-372.

Tillberg, M. et al., 2021. Reconstructing craton-scale tectonic events via in situ Rb-Sr geochronology of poly-phased vein mineralization. Terra Nova, 33(5): 502-510.

Tillberg, M. et al., 2020. In situ Rb-Sr dating of slickenfibres in deep crystalline basement faults. Scientific Reports, 10(1).

Vermeesch, P., 2018. IsoplotR: A free and open toolbox for geochronology. Geoscience Frontiers, 9(5): 1479-1493.

Villa, I.M., De Bièvre, P., Holden, N.E., Renne, P.R., 2015. IUPAC-IUGS recommendation on the half life of 87Rb. Geochimica et Cosmochimica Acta, 164: 382-385.

Wang, C.Y. et al., 2022. Advances in in-situ Rb-Sr dating using LA-ICP-MS/MS: applications to igneous rocks of all ages and to the identification of unrecognized metamorphic events. Chemical Geology, 610.

Woodhead, J.D., Hergt, J.M., 2001. Strontium, Neodymium and Lead Isotope Analyses of NIST Glass Certified Reference Materials: SRM 610, 612, 614. Geostandards Newsletter, 25(2-3): 261-266.

Zack, T., Hogmalm, K.J., 2016. Laser ablation Rb/Sr dating by online chemical separation of Rb and Sr in an oxygen-filled reaction cell. Chemical Geology, 437: 120-133.