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$^{40}\text{Ar}/^{39}\text{Ar}$ age of the Rotoiti Breccia and Rotoehu Ash, Okataina Volcanic Complex, New Zealand, and identification of heterogeneously distributed excess ^{40}Ar in supercooled crystals.

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Abstract

Co-magmatic granitoid clasts erupted as part of the Rotoiti Ignimbrite (Rotoehu Tephra) contain euhedral K-feldspar and biotite crystals that protrude into miarolytic cavities and show textural evidence for growth in super-cooled conditions, thus are interpreted as growing during eruption. $^{40}\text{Ar}/^{39}\text{Ar}$ stepped heating experiments on single K-feldspar crystals reveal the presence of heterogeneously distributed excess ^{40}Ar , preferentially released at lower temperature steps (most likely from fluid/melt inclusions), which cannot reliably be characterised by, or corrected for using isotope correlation diagrams due to mixing between three reservoirs of ^{40}Ar (radiogenic, atmospheric and excess). This excess ^{40}Ar component is common, but not ubiquitous, and an age population unmixing algorithm applied to single-crystal fusion data identifies a younger group of K-feldspar and biotite crystals that appear to be largely unaffected by excess ^{40}Ar . This population gives a statistically robust weighted mean age of 47.4 ± 1.5 ka (1σ , $n = 13$) and an indistinguishable inverse isochron age of 50 ± 3 ka for this historically difficult to date eruption. The weighted mean age is significantly younger than previous age estimates of the Rotoiti eruption obtained by K/Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ dating of bracketing lavas, but is indistinguishable from recent ^{14}C and (U-Th)/He dates and estimates based on orbital tuning and sedimentation rates constrained by ^{14}C ages.

Keywords

Rotoiti ignimbrite eruption; $^{40}\text{Ar}/^{39}\text{Ar}$; excess- ^{40}Ar ; Taupo Volcanic Zone

1. Introduction

The Rotoiti ignimbrite and Rotoehu ash, erupted from the Okataina Caldera in the Taupo Volcanic Zone (TVZ) and immediately followed by the eruption of the Earthquake Flat (EQF) ignimbrite, is an important regional stratigraphic marker on the North Island of New Zealand and in the SW Pacific Ocean which has been used to correlate numerous stratigraphic sections both onshore and offshore (e.g. Berryman, 1992; Molloy et al., 2008; Nilsson et al., 2011; Shane et al., 2006). It occurs at the base of a remarkably well constrained tephra record in which all deposits have been correlated to their source vents and their distribution is well known (Shane, 2000) and so an accurate age for this deposit is particularly important for calculating both sedimentation rates and magma production and eruption rates in the TVZ and surrounding areas. Furthermore, the climatic conditions before and after the eruption are well constrained and the ash is interpreted to have been deposited during an interstadial, most likely in the middle of Marine Isotope Stage (MIS) 3 (Mcglone et al., 1984; Shane and Sandiford, 2003). However, despite 45 years of study and numerous attempts to date the eruption, the age of the Rotoehu ash still remains controversial, with recent published ages ranging from ~45 to 61 ka. In this paper we present $^{40}\text{Ar}/^{39}\text{Ar}$ stepped heating and total fusion data for single crystals of K-feldspar and biotite from co-magmatic granitoid lithic clasts erupted as part of the Rotoiti ignimbrite and show that the eruption most likely took place at ~ 47 ka.

1.1 Geological context

The 60 km wide Taupo Volcanic Zone (TVZ) extends ~300 km north-eastwards from the centre of the North Island of New Zealand into the Bay of Plenty and the south Pacific Ocean (Figure 1). Volcanism in the TVZ began at ~2 Ma, becoming dominated by silicic volcanism after ~1.6 Ma and it is currently the most active region of silicic volcanism on Earth, with rhyolite eruption rates of $3.8 \text{ km}^3 \text{ ka}^{-1}$ (over the last 1.6 Ma). There are at least 8 caldera complexes that have been active over the lifetime of the TVZ, with at least 34 caldera forming eruptions identified as having occurred since 1.6 Ma (Wilson et al., 1995). The Okataina caldera complex (also referred to as the Haroharo Caldera complex, Charlier et al., 2003; Shane et al., 2012; Smith et al., 2010) is one of the most productive silicic volcanoes known with rhyolite production rates quoted as being $2.5 \text{ km}^3 \text{ ka}^{-1}$ over the last 65 ka (Wilson et al., 1995). The Rotoiti ignimbrite (also referred to as the

57 Rotoiti breccia) and Rotoehu ash were produced during the most recent caldera collapse eruption of the
58 Okataina caldera. The eruption began with an explosive basaltic eruption, producing the Matahina Tephra
59 (Pullar and Nairn, 1972) and was immediately followed by the Rotoiti eruption which produced non-welded
60 ignimbrite, interbedded with and overlain by phreatomagmatic ash, with the combined ignimbrite and ash
61 equating to a magma volume of at least 80 km³ (Wilson et al, 2007). The Rotoiti eruption was followed
62 almost immediately (within months) by the smaller volume (7 km³ of magma) Earthquake Flat ignimbrite
63 and associated Rifle Range ash (Nairn and Kohn, 1973; Wilson et al., 2007), which is generally considered to
64 originate from the Kapenga caldera complex, although Burt et al. (1998) suggested that the EQF vent
65 lineament represents a cryptic ring-shaped structural boundary of the Okataina volcanic centre (Figure 1B).

Fig. 1. (A) – Map showing the tectonic setting of the Taupo Volcanic Zone (TVZ), related to the subduction of the Pacific plate beneath the Australian plate, with onshore (white diamonds) and offshore (black diamonds) occurrences of the Rotoiti Ignimbrite and / or Rotoehu ash (Allan et al., 2008; Berryman, 1992; Danišík et al., 2012; Molloy et al., 2009; Nairn and Kohn, 1973; Santos et al., 2001; Shane et al., 2006; Shane and Sandiford, 2003). Square box shows the location of Figure. 1B. (B) – Structural map of the Okataina Caldera, the source of the Rotoiti eruption (after Charlier and Wilson, 2010). Dashed line represents the cryptic structural boundary of the Okataina caldera as suggested by Burt et al. (1998).

65 Plutonic lithic fragments brought to the surface during ignimbrite eruptions have been observed in many
66 TVZ volcanic deposits (Brown et al., 1998; Burt et al., 1998; Charlier et al., 2003; Ewart and Cole, 1967;
67 Shane et al., 2012). However, a notable class of felsic plutonic clasts contained in a lithic lag breccia facies
68 of the Rotoiti ignimbrite contain volcanic glass, indicating that they were incompletely crystallised at depth
69 and so are referred to as granitoids (Brown et al., 1998; Burt et al., 1998). The most common type of these

70 granitoid clasts, Group 1 granitoids (the subject of this study), tend to be highly friable, exhibit quench
71 textures, such as volcanic glass, micrographic intergrowths and miarolytic cavities lined with euhedral
72 crystals, and often contain two populations of biotite (Brown et al., 1998; Burt et al., 1998; Charlier et al.,
73 2003). Importantly, the glass in these granitoid fragments often co-exists with euhedral crystals, implying
74 that the glass represents quenched residual melt, rather than melt infiltration and remobilisation of a
75 previously solidified magma body, which would result in rounded and resorbed crystals (Brown et al., 1998;
76 Burt et al., 1998). Based on contrasting chemical and isotopic signatures, the granitoid clasts are generally
77 considered to be co-magmatic, rather than cognate or xenolithic, to the Rotoiti ignimbrite magma, forming
78 from a spatially close but petrogenetically distinct magma batch (possibly derived from the Matahina
79 magmatic system) that was emplaced at a high crustal level and subsequently disturbed during the caldera-
80 collapse phase of the Rotoiti eruption (Brown et al., 1998; Burt et al., 1998; Charlier et al., 2003; Shane et
81 al., 2005). Cooling and crystallisation of the Group 1 granitoids is generally considered to have taken place
82 in at least two stages, with most crystallisation taking place at 10-15 km depth, followed by volatile-loss,
83 undercooling and crystallisation at < 3 km, associated with upheaval caused by migration of the Rotoiti
84 magma towards the surface (Brown et al., 1998; Burt et al., 1998).

85

86 **1.2 Previous age estimates for the Rotoiti eruption**

87 The range of published ages for the Rotoiti eruption is given in Table 1, along with pertinent details, and in
88 Figure 2 (all ages in this paper are quoted as $\pm 1\sigma$, where known). The earliest attempts to assign an age to
89 the Rotoiti eruption utilised radiocarbon dating and were plagued by difficulties relating to the age limit for
90 ^{14}C dating (generally considered to be ~40-50 ka) and contamination with younger carbon material
91 (Froggatt and Lowe, 1990; Grant-Taylor and Rafter, 1971; Lowe and Hogg, 1995; Nairn and Kohn, 1973;
92 Nathan, 1976; Pillans and Wright, 1992; Pullar, 1976; Pullar and Heine, 1971; Shane, 2000; Thompson,
93 1968a; Vucetich and Pullar, 1969; Whitehead and Ditchburn, 1994). For many years, Wilson et al.'s (1992)

Method	Unit	Age (ka) $\pm 1\sigma$	Notes	References
^{14}C (pre-2000)	Rotoiti breccia and ash	31 - > 41	Ages at limit of detection and contaminated by younger carbon.	1-8, 10, 12, 17, 18
^{238}U - ^{230}Th disequilibrium	Rotoehu ash	71 $\pm$ 6	Data considered invalid by refs 10,18	9
Electron spin resonance	Rotoiti breccia	45.2 $\pm$ 8.2	Refs 9 and 10 suggest data may be invalid due to U-Th disequilibrium.	11
Marine sedimentation rates	Rotoehu ash	~55	Tephra not conclusively identified	12
K/Ar	Mayor island lava bracketing Rotoehu ash	64 $\pm$ 4	Overlying lava = 67 $\pm$ 11 ka. Underlying lava = 63 $\pm$ 5 ka	13
Stratigraphic age	Extrapolation between marine terrace ages formed pre and post deposition	52 $\pm$ 7	Ages of bracketing terraces = 40 and 59 ka. Ages of terraces refined to ~43 and 61 ka respectively by ref 21.	14,15
Amino acid racemization	Palaeosols bracketing Rotoiti breccia and ash	~61		16
Optical Luminescence Dating	Underlying and overlying palaeosols from 2 sections	42 $\pm$ 8 - 34 $\pm$ 3 44 $\pm$ 3 - 30 $\pm$ 2		19
^{14}C -AMS	Wood below the Rotoehu ash	43.2 $\pm$ 0.6		20
^{238}U - ^{230}Th disequilibrium	Rotoehu ignimbrite – xenolith: Rotoehu ignimbrite - pumice	57 $\pm$ 8 > 29 $\pm$ $^{21}_{17}$	Whole rock – magnetite – biotite Zircons	22
Lake sedimentation rates	Rotoehu ash	44.3	Palynology suggests Rotoehu ash deposited during MIS 3, i.e. between 59.1 and 29.0 ka	23
Lake sedimentation rates	Rotoehu ash	48.9	Composite depth scale calibrated by overlying ^{14}C dating of tephra	24
Marine sedimentation rates	Rotoehu ash	~45	Multiple deep sea sediment cores with chronology based on ^{14}C and Th/U- ^{14}C ages of coral and foraminifera.	25
Combined K-Ar and $^{40}\text{Ar}/^{39}\text{Ar}$	Mayor island lava bracketing Rotoehu ash	61.0 $\pm$ 1.4	Ar/Ar dates from crystals from Rotoiti and EQF eruptions give ages of 47 - 125 ka	26
Orbitally tuned marine sediment	Rotoehu ash	45.1		27
Lake sedimentation rates	Rotoehu ash	46-52	Sedimentation rates extrapolated from the between overlying Maketu and Tahuna tephra layers	28
^{14}C -AMS	Underlying / Overlying Rotoehu ash	47.5 $\pm$ 2.1 44.8 $\pm$ 0.3	Ages calibrated to calendar years BP	29
(U-Th)/He	Rotoiti Breccia / Earthquake Flat Pumice	45.1 $\pm$ 3.3 45.1 $\pm$ 2.9		29

Table 1. Published age estimates of the Rotoiti eruption, in order of publication. 1 (Thompson, 1968b), 2 (Vucetich and Pullar, 1969), 3 (Pullar and Heine, 1971), 4 (Grant-Taylor and Rafter, 1971), 1971, 5 (Nairn and Kohn, 1973), 6 (Nathan, 1976), 7 (Pullar, 1976), 8 (Mcglone et al., 1984), 9 (Ota et al., 1989), 10 (Froggatt and Lowe, 1990), 11 (Buhay et al., 1992), 12 (Pillans and Wright, 1992), 13 (Wilson et al., 1992), 14 (Berryman, 1992), 15 (Berryman, 1993), 16 (Kimber et al., 1994), 17 (Whitehead and Ditchburn, 1994), 18 (Lowe and Hogg, 1995), 19 (Lian and Shane, 2000), 20 (Santos et al., 2001), 21 (Chappell, 2002), 22 (Charlier et al., 2003), 23 (Shane and Sandiford, 2003), 24 (Nilsson et al., 2011), 25 (Shane et al., 2006), 26 (Wilson et al., 2007), 27 (Allan et al., 2008), 28 (Molloy et al., 2008), 29 (Danišik et al., 2012)

age of 64 ± 4 ka, based on K/Ar dating of overlying (67 ± 11 ka) and underlying (63 ± 5 ka) obsidian lava flows on Mayor Island was considered to be the most reliable age for the Rotoiti eruption. This age was subsequently revised to 61.0 ± 1.4 ka based on a $^{40}\text{Ar}/^{39}\text{Ar}$ stepped heating plateau age of 58.5 ± 1.1 ka for the overlying Mayor Island obsidian lava flow and supported by stepped heating experiments on biotite and plagioclase from the Rotoiti and EQF ignimbrites, which showed a high level of xenocrystic contamination (Wilson et al., 2007). Indeed, ^{238}U - ^{230}Th disequilibrium dating of both Rotoiti pumice and granitoid clasts and of the EQF ignimbrite indicates a prolonged crystallisation history, with isochron and weighted mean ages ranging from 51 ± 14.5 ka to 122^{+9}_{-8} ka (Charlier et al., 2003; Charlier and Wilson, 2010; Danišik et al., 2012). Danišik et al. (2012) addressed the problem of age-inheritance in zircons by carrying out (U-Th)/He dating, a method that has the advantage of avoiding potential pre-eruptive inheritance issues because of the high diffusion rate of ^4He at magmatic temperatures. They produced indistinguishable ages of 45.1 ± 3.3 and 45.1 ± 2.9 ka for the Rotoiti and EQF eruptions respectively. They also, along with Santos et al. (2001) addressed earlier problems with ^{14}C dating of the Rotoiti eruption by utilising high-sensitivity Accelerator Mass Spectroscopy (AMS) and improved sample preparation procedures to remove contaminating younger carbon, producing ^{14}C ages for material underlying and overlying the Rotoehu ash that are consistent with the (U-Th)/He dates. This younger date is also consistent with numerous age estimates (generally 45-50 ka) based on marine and lake sedimentation rates, calibrated by ^{14}C dating of younger tephras (Allan et al., 2008; Molloy et al., 2009; Nilsson et al., 2011; Pillans and Wright, 1992; Shane et al., 2006; Shane and Sandiford, 2003) and with Optical Luminescence (OSL) dating of palaeosols above and below the Rotoiti deposits. A slightly older (but with larger errors, overlapping most other age estimates) stratigraphic age for the Rotoehu ash of 52 ± 7 ka was proposed by Berryman, (1992, 1993) based on correlation of sediments bound by ages of marine terraces. The bounding terrace ages (40 ka and 59 ka) were based on correlation with marine terraces at the Huon Peninsula, New Guinea, dated by ^{14}C and $^{230}\text{Th}/^{234}\text{U}$ dating of corals (Chappell and Shackleton, 1986). Wilson et al. (2007) noted an updated age for the terraces (Chappell, 2002) and suggested that, according to Berryman's correlations, the Rotoiti eruption must have occurred between 72.8 ± 1.1 and 51.8 ± 0.4 ka. However, these ages are based on incorrect identification of the relevant marine terraces, probably due to inconsistencies in terrace naming

121 between Chappell and Shackleton (1986) and Chappell (2002); the correct age for the older terrace is 61.4
 122 ka and the younger terrace was not re-dated, but is likely ~43 ka, based on extrapolation between older
 123 (43.9 ka) and younger (42.1 ka) terraces, suggesting that the Rotoiti eruption took place between 61.4 and
 124 43 ka.

Figure 2. Schematic diagram showing ages published for the Rotoiti eruption. Vertical bars represent 1 standard deviation of published ages, or set as arbitrary squares where errors are not available (12, 16, 23-25, 27). Numbers refer to the references cited in Table 1. The horizontal grey bar represents the age ± 1 σ determined in this study.

124 **2. Samples and methodology**

125 Despite evidence of pre-eruption age zircons and thus an extended crystallisation history of Group 1
 126 granitoid fragments (Charlier et al., 2003), the abundant quench textures which they exhibit indicate that at
 127 least part of the clasts crystallised during eruption. Sample 103/1, collected from the same granitoid block
 128 as sample 103/2, analysed by Charlier et al. (2003), contains abundant glass and miarolytic cavities lined
 129 with euhedral K-feldspar, quartz and biotite, which we interpret as having crystallised and quenched during
 130 eruption.

131 A polished thin section was prepared by impregnating a split of the sample with blue epoxy to highlight the
132 miarolytic cavities and porosity of the sample. This section (Figure 3) exhibits many of the quench features
133 identified by Burt et al. (1998) and Charlier et al. (2003), such as granophyric texture, along with euhedral
134 quartz and K-feldspar crystals forming linings to the miarolytic cavities. Optical petrography of the euhedral
135 K-feldspars shows that they are highly strained, exhibiting strongly developed cleavage planes, patchy,
136 streaky and undulose extinction and, in some crystals, kinked cleavage planes and fine-scale structures in
137 the core of the crystal, that appear streaky under both PPL and XPL (Figure 3B). These structures are similar
138 in appearance to plagioclase-alkali feldspar intergrowths, and patchy extinction and sector zoning formed
139 during sanidine crystallisation from an undercooled melt (Lofgren and Gooley, 1977). We interpret these
140 feldspar textures as representing a combination of crystallisation during melt undercooling, and
141 deformation during shearing processes during mobilisation and eruption, a process considered to be
142 ubiquitous in the Group 1 granitoids (Brown et al., 1998; Burt et al., 1998).

143 Element mapping and semi-quantitative spot analyses were carried out on the polished section using a
144 Bruker-nano M4 Tornado benchtop micro-XRF system. Analysis conditions, a summary of the technique and
145 all semi-quantitative data are given in the supplementary information and Supplementary Data Table S1. A
146 major element map displaying Si, K and Fe is shown in Figure 3A. The large area (1.5 × 2.5 cm) covered by
147 the x-ray map reveals that many of the granophyric intergrowths radiate towards the miarolytic cavities,
148 often terminating with euhedral quartz and K-feldspar crystals that project into the cavity.

149 A semi-quantitative chemical composition profile across a euhedral K-feldspar crystal (Figure 3D) suggests
150 cryptic normal zoning, with relative Na-enrichment in the core and K-enrichment at the rim. Spot analyses
151 of the fine-scale structures in Figure 3b indicate a relative enrichment of CaO and Na₂O and depletion of
152 K₂O, consistent with our interpretation that they represent plagioclase – K-feldspar intergrowths during
153 undercooling.

155

156 **Figure 3. A) μ -XRF element map from a polished section of a miarolytic cavity in a granitoid clast.**
157 **Elements are displayed as Si = red, K = green and Fe = blue, therefore quartz displays as bright red, K-**
158 **feldspar as green, plagioclase as dark red and biotite and Fe-oxides as blue. White boxes show the**
159 **positions of panels B (left) and C (right). B) XPL photomicrograph of an alkali feldspar crystal protruding**
160 **into the miarolytic cavity. The white dotted line highlights fine-scale textures interpreted as plagioclase –**
161 **K-feldspar intergrowths. Q = quartz crystals. C) XPL photomicrograph of an alkali feldspar crystal that**
162 **grew into the miarolytic cavity. The crystal displays streaky and patchy extinction. The line a-b shows the**
163 **position of the semi-quantitative chemical profile shown in panel (D) (see supplementary information for**
164 **details). In the photomicrographs, white arrows highlight regions in the crystals rich in fluid and / or**
165 **magmatic inclusions. Blue colouration is from impregnation during section preparation and highlights the**
166 **permeable nature of the granitoids.**

167

168 0.5-1 mm euhedral K-feldspar and 1-2 mm biotite crystals were hand-picked from miarolytic cavity linings
169 of the kind illustrated in Figure 3A and prepared for irradiation for Ar-isotope analysis using standard
170 techniques (see supplementary information). Given the likely extended crystallisation history of the
171 granitoid clasts, all Ar-isotope analyses were carried out on single crystals to enable identification of any
172 crystals that record pre-eruptive ages and prevent mixing of crystal populations. We carried out a

173 combination of single grain fusion and single grain stepped heating experiments on both K-feldspar and
174 biotite crystals using a 50 W Synrad CO₂ laser. Gas clean-up was through an all-metal extraction line with a -
175 130 °C cold trap, to remove H₂O, and two water-cooled SEAES GP-50 getters to absorb reactive gases. The
176 Ar-isotope analyses were carried out on a Nu Instruments Noblesse multi-collector noble gas mass
177 spectrometer. Analytical procedures, previously documented in Brumm et al., (2010) are detailed in the
178 supplementary information file and all results, correction factors and constants are given in the
179 supplementary data file. As previous studies on similar material (Wilson et al., 2007) had reported high
180 levels of contamination with Cl, which can cause an isobaric interference with ³⁶Ar in the mass
181 spectrometer by formation of ¹H³⁵Cl, ³⁵Cl was measured in addition to the Ar-isotope analyses to monitor
182 for Cl contamination, none of which was observed.

183 **3. ⁴⁰Ar/³⁹Ar Results**

184 Results of the Ar-isotope single crystal analyses are given in supplementary Tables 2 and Figures 4 - 7. K-
185 feldspar single grain fusion ages (excluding data with blank-corrected ⁴⁰Ar yields of less than 0.5 mV
186 (~30,000 cps) and zero ⁴⁰Ar* yields; n = 27) range from 31 ± 5 ka to 125 ± 18 ka, indicating that some grains
187 record pre-eruption model ages, i.e. they are either xenocrystic or contain excess ⁴⁰Ar. Biotite single grain
188 fusion ages (n=4) range from 39 ± 8 ka to 57 ± 6 ka. An isotope correlation diagram plotting all of the single
189 crystal fusion data (Figure 5) gives an inverse isochron age of 55.3 ± 1.8 ka.

190 Stepped heating experiments were carried out on 5 K-feldspar and 1 biotite crystals, yielding 3 steps for the
191 K-feldspars and 4 steps for the biotite, although some of these steps produced exceptionally low ⁴⁰Ar, ⁴⁰Ar*
192 and / or ³⁹Ar gas yields. The individual step heating data yielded apparent ages from 39 ± 8 ka to 105 ± 16
193 ka.

194 Three of the five K-feldspar crystals gave high apparent ages for the first temperature step (up to 105 ka)
195 and exhibit decreasing age with increasing temperature (e.g. 2608-02, Figure 4) while a fourth followed the
196 same pattern but the first and final temperature steps yielded < 0.5 mV ⁴⁰Ar and so have been discounted.
197 Isochrons could not be calculated for these crystals. Stepped heating of K-feldspar 2608-04 yielded

198 consistent ages for all three temperature steps, giving a 3-step "plateau" age of 50 ± 4 ka (Figure 4) and a 3-
 199 point isochron age of 51 ± 0.5 ka ($^{40}\text{Ar}/^{36}\text{Ar} = 298 \pm 3$, MSWD = 0.5, $p = 0.48$). Stepped heating was
 200 attempted on one biotite crystal using 4 temperature (laser power) steps. The first two of these steps
 201 released gas with an $^{40}\text{Ar}/^{36}\text{Ar}$ composition within uncertainty of the atmospheric ratio of 298.56, and can
 202 be attributed to the release of loosely adhering atmospheric argon from gentle heating of the crystal.

203

204 **Figure 4. $^{40}\text{Ar}/^{39}\text{Ar}$ age spectra from stepped heating experiments on single K-feldspar crystals. Crystal**
 205 **2608-02 shows a gas release pattern of decreasing model age with increasing temperature and suggests**
 206 **that excess ^{40}Ar is present in fluid and magmatic inclusions in the crystals. By contrast, crystal 2608-04**
 207 **exhibits a flat release spectrum and younger age, suggesting that it is either unaffected by, or at least less**
 208 **influenced by excess ^{40}Ar . Error boxes on the spectra are 2σ and all quoted errors are 1σ .**

209

210 $^{40}\text{Ar}/^{39}\text{Ar}$ ages from stepped heating of individual crystals that vary beyond normal analytical uncertainties
 211 can be interpreted in terms of excess ^{40}Ar , inherited ^{40}Ar in xenocrystic or antecrystic cores, or as ^{39}Ar loss
 212 due to recoil. These possibilities are discussed below.

213 4. Interpretation of variable model $^{40}\text{Ar}/^{39}\text{Ar}$ ages

214 4.1 Inherited $^{40}\text{Ar}^*$.

215 Inherited $^{40}\text{Ar}^*$ is a possible reason for older ages observed in both stepped heating and fusion analyses.
 216 The granitoid clasts are interpreted as having crystallised in multiple stages (Brown et al., 1998; Burt et al.,

1998) and contain zircons that record pre-eruption ages (Charlier et al., 2003) and so it would be expected that these clasts contain antecrystic material. However, we purposefully selected crystals lining miarolytic cavities in the clasts to avoid antecrysts retaining $^{40}\text{Ar}^*$ older than the eruption. The bulk of sample 103/1 has a sugary, friable texture, indicative of gas exsolution and quenching of interstitial melt to form volcanic glass. The glass was considered by Brown et al., (1998) to be interstitial melt, rather than infiltrated melt or partial melt during reheating based on textural and chemical analysis. The presence of glass quenched from interstitial melt indicates that the granitoid remained partially molten until eruption and will have sustained elevated temperatures; Brown et al., (1998) suggested a feldspar thermometry crystallisation temperature of 700 °C for the later stage, supercooled crystals. Granophyric texture (Figure 3) and miarolytic cavities are further evidence that this sample crystallised and quenched during transport to the surface (Brown et al., 1998; Burt et al., 1998) and it is difficult to envisage a scenario where miarolytic cavities and glass could form in the subsurface and be retained over geochronologically significant timescales without being modified.

If the crystals we analysed did form thousands of years before the eruption and retained a portion of their $^{40}\text{Ar}^*$, we would expect this to be reflected in the age spectra produced by stepped heating experiments. Inherited $^{40}\text{Ar}^*$ would diffuse out of the crystal while ever the crystal is held at elevated temperature in the subsurface and / or during eruption and so the highest concentration of $^{40}\text{Ar}^*$ would be in the core of the crystal. This would manifest on age spectra as younger ages in the early steps and older ages in the latter steps. This pattern is opposite to what is observed for stepped heating of single feldspar crystals, which produce the oldest ages in the earliest steps.

As a further check, we carried out diffusion modelling to assess whether a feldspar that crystallised as part of a partially molten mush, thousands of years before the eruption, would retain any $^{40}\text{Ar}^*$ and thus give older ages. We considered a simplified scenario where an Ar-bearing feldspar was held at 700 °C and modelled the fractional Ar loss experienced by the crystal. We assumed a spherical crystal of radius of 0.5 mm (the largest crystals analysed), $D_0 = 0.0098 \text{ cm}^2 \text{ s}^{-1}$ and $E = 44 \text{ kcal mol}^{-1}$ (Foland, 1994) and used the fractional loss equations given in McDougall and Harrison (1999). Under these conditions, 100% of the Ar in

243 the crystal would have been lost after just 40 years. Feldspars of this size that crystallised thousands of
244 years before the eruption would only retain a significant proportion (>50%) of their $^{40}\text{Ar}^*$ at temperatures <
245 500 °C; the evidence for interstitial melt in the granitoid clasts is not consistent with such low
246 temperatures.

247

248 **4.2 Recoil of ^{39}Ar**

249 Recoil of ^{39}Ar during neutron irradiation may result in ejection of ^{39}Ar atoms from the crystal lattice and can
250 be a problem for samples where the grain size is approaching the ^{39}Ar recoil distance (partial depletion
251 layer thickness of 0.7 μm - (Jourdan et al., 2007)). Recoil typically manifests on age spectra as a stepwise
252 decrease in age with increasing temperature, similar to that observed during stepped heating of our
253 individual feldspar crystals; gas release from early temperature steps is dominated by that from the smaller
254 grain sizes most affected by recoil and the relative depletion in ^{39}Ar relative to $^{40}\text{Ar}^*$ results of over-
255 estimation of the $^{40}\text{Ar}/^{39}\text{Ar}$ age.

256 In the case of our Rotoiti samples, individual crystals are ~ 1mm diameter or larger; many appear fractured
257 in thin section (Fig. 3B) but these fracture domains are still tens of microns in diameter and thus unlikely to
258 be affected by recoil. It is possible that the observed patches of streaky extinction and very fine lamellae in
259 some of the K-feldspar crystals represent structures that could facilitate recoil of ^{39}Ar , but these often occur
260 as discrete patches interspersed with areas that are more homogenous and it is likely that such a scenario
261 would not produce the “classic” decreasing age spectrum associated with recoil.

262 **4.3 Excess ^{40}Ar**

263 Excess ^{40}Ar hosted in melt or fluid inclusions may produce age spectra with older apparent ages in the early
264 temperature steps; decrepitation of the inclusions releases the excess ^{40}Ar during the earliest heating
265 stages and contributes to the classic “saddle-shaped” age spectrum associated with excess ^{40}Ar .

266 The age spectra produced by stepped heating of individual crystals (Fig. 4) are consistent with fluid /
267 magmatic inclusion-hosted excess ^{40}Ar . Furthermore, many K-feldspars in sample 103/1, contain an
268 abundance of magmatic and / or fluid inclusions (Figure 3).

269 The stepped heating data suggest that this excess ^{40}Ar is present in varying degrees in many, but not all of
270 the crystals; the flat release and younger apparent age of crystal 2608-04 suggests that it contains little or
271 no excess ^{40}Ar . If excess ^{40}Ar is inhomogeneously distributed within a sample (e.g. in clusters of fluid or
272 magmatic inclusions, as observed in the photomicrographs in Figure 3), especially if it is decoupled from an
273 atmospheric component (i.e. 3-way mixing between radiogenic, atmospheric and excess Ar), it can be
274 difficult or impossible to identify using isotope correlation diagrams as regressions of the data will tend to
275 yield an atmospheric intercept and an apparent age that is too old (Kuiper, 2002).

276 **4.4 Eruption age vs. excess ^{40}Ar age**

277 Plotting the stepped heating data from all six (5 K-feldspar, 1 biotite) crystals onto an isotope correlation
278 diagram produces an apparent age of 54 ± 3 ka with a trapped $^{40}\text{Ar}/^{36}\text{Ar}$ content of 298.9 ± 1.6 ($n=14/16$,
279 two data points automatically rejected by the Mass Spec software). In Figure 5 the data are plotted
280 according to their temperature step; low temperature steps (light grey) tend to lie below the isochron line
281 while the higher temperature steps (black) lie on or above the line. The isochron has an atmospheric
282 intercept, despite an excess ^{40}Ar component clearly being identified on age spectra. Such a distribution of
283 data points is consistent with a scenario involving mixing of atmospheric, radiogenic and excess ^{40}Ar , as
284 described by (Kuiper, 2002). Data points not affected by excess ^{40}Ar would define an isochron formed by a
285 mixing line between radiogenic and atmospheric end-members, with an atmospheric intercept.
286 Heterogeneous incorporation of excess ^{40}Ar , as a source of trapped Ar additional to atmosphere, shifts the
287 data points downwards and to the left of the isochron line. This has the net effect of increasing the slope of
288 the calculated isochron line, resulting in an older age, whilst maintaining an atmospheric intercept; such an
289 apparent isochron is an artefact and does not represent mixing between a single trapped and radiogenic
290 end members (Kuiper, 2002). The high MSWD (2) suggests that the scatter of the data is greater than would
291 be expected based on the errors on the individual data points and this is consistent with this interpretation

292 of variably-distributed excess ^{40}Ar . Inspection of the stepped heating isochron shows that it is dominated by
 293 data from the middle and high temperature steps. Given that the middle temperature steps may still
 294 contain excess ^{40}Ar , this isochron age is considered to be an over-estimate and an upper limit of the
 295 eruption age.

296

297 **Figure 5: Isotope correlation diagrams created using the software Mass Spec (Al Deino, Berkeley**
 298 **Geochronology Center). Isochron ages were calculated invoking an automated data filtering process to**
 299 **eliminate outliers on the basis of their large contribution to the weighted sum of squares of the linear**
 300 **regression of the data. Top panel: Isotope correlation diagram combining stepped heating data from 6**
 301 **individual crystal stepped heating experiments: 5 K-feldspar (ellipses) and 1 biotite (squares). The first**
 302 **two biotite temperature steps were dominated by air and have been excluded from the diagrams for**
 303 **clarity. Light grey symbols = low temperature steps ($\sim 0.5\text{W}$), dark grey symbols = medium temperature**
 304 **steps ($\sim 1.5\text{ W}$) and black symbols = high temperature steps ($4\text{-}10\text{ W}$). Bottom panel: Isotope correlation**
 305 **diagram of the single crystal fusion data. Ellipses = K-feldspar data, squares = biotite data. Filled symbols**
 306 **show the data contributing to the grey isochron line (55.3 ± 1.1 ka) which is based on all of the single**
 307 **crystal fusion data. Black symbols represent the data points thought to be least-contaminated by excess**
 308 **^{40}Ar (see main text on the unmixing model) and form an isochron with an age of 50 ± 3 ka.**

309 Next we consider whether the single crystal total fusion data can improve our estimate of the eruption age.
310 If we assume that each crystal contains a different amount of excess ^{40}Ar , and that some crystals contain
311 little or no excess ^{40}Ar as shown by the step-heating experiments, we can treat the dataset as a mixture of
312 populations with different apparent ages, and that the youngest coherent age population represents the
313 crystals least contaminated with excess ^{40}Ar and is a best-estimate of the eruption age.

314 To identify the youngest coherent age population, ages were initially analysed using the Isoplot unmixing
315 tool (Ludwig, 2008), which is based on Sambridge and Compston's (1994) algorithms for deconvoluting
316 mixtures of similar age zircon populations. These algorithms aim to determine the true number of age
317 components, their age values, and their relative proportions using an iterative procedure; the exact values
318 of the true age and relative proportions of the different populations are not directly recoverable and,
319 instead, the model makes a best estimate of the ages and proportions, based on a maximised likelihood of
320 the data representing multiple age components (Sambridge and Compston, 1994). The procedure begins
321 with a guess of the number of age components (age populations) and returns an estimate of the ages (with
322 error), relative proportions of those components and likelihood that the data are best described by those
323 components (the likelihood is returned as the inverse log of the likelihood – the relative misfit parameter).
324 The procedure is repeated using a different number of components until a minimum value for the relative
325 misfit parameter is achieved. The model assumes that all populations have a Gaussian distribution. The
326 relative proportions are calculated as the ratio of the areas beneath each population's distribution curve
327 (Figure 6) (Sambridge and Compston, 1994).

328 Use of this model to fully assess our single crystal fusion data is a little problematic because of the
329 requirement for a Gaussian age distribution; while we expect the analyses not contaminated with excess
330 ^{40}Ar to approximate a Gaussian distribution, this is unlikely for the variable contaminated crystals and the
331 actual spread of ages in this population is likely to include a substantial tail to older ages. To maximise the
332 likelihood of the model giving meaningful results, we attempted to remove the non-Gaussian tail from the
333 excess ^{40}Ar contaminated population by excluding all ages greater than Wilson et al's (1992) initial age
334 estimate of 64 ka. We also excluded the three youngest data (all of which gave geologically unreasonable

ages of <32 ka). For the remaining 22 data points, a minimum value for the relative misfit parameter (1.044) was achieved by invoking 2 populations with the youngest population estimated at 47.9 ± 2.1 ka and formed by 55% of the data and the older population estimated at 59.6 ± 3.6 ka and formed by 45% of the data (Figure 6).

339

Figure 6: Sambridge and Compston's (1994) unmixing model for the single crystal fusion $^{40}\text{Ar}/^{39}\text{Ar}$ age data. Using Isoplot, the unmixing model suggests two populations are present: a younger population (estimated age 47.9 ± 2.1 ka, 55%) and an older, excess ^{40}Ar contaminated population (estimated age 59.6 ± 3.6 ka, 45%). The relative proportions of the populations are calculated by ratioing the area beneath the population curves. Where the curves overlap (grey shading), it is difficult to conclusively assign individual data points to each population. The diagram shows a hypothetical analysis with an age of 53 ka (dashed line) - the probability of this analysis belonging to the older population (f_2) is greater than the probability of it belonging to the younger population (f_1), but it could belong to either.

This unmixing model was used to select analyses belonging to the youngest population from which to calculate a weighted average. Assigning each individual analysis to a population becomes difficult for ages that are described by both populations (shaded area on Figure 6). All ages > 52 ka (the point where the two population distribution curves cross) have a higher probability of belonging to the older population than the younger population (see case study of a hypothetical 53 ka data point in Figure 6). Simply assuming that the youngest 55% of the data (i.e. the youngest 12 analyses) represent the youngest population is likely to exclude data that do belong to the younger population, but have ages > 52 ka. Instead we consider the range of ages beneath the young population distribution curve as a guide to selecting data that are not

356 contaminated by excess ^{40}Ar and use 55 ka as an upper limit for data belonging to the young population.

357 Using this criterion, 13 out of the 22 analyses were assigned to the young population (39 ± 8 to 52 ± 4 ka). A

358 weighted average of these data gives an age of 47.4 ± 1.5 ka with a statistically acceptable MSWD

359 (according to the criteria of Wendt and Carl, 1991) of 0.58 for $n = 13$ and a probability of fit of 0.86. Figure 7

360 shows this weighted average in the context of the individual data, the distribution curves for the population

361 unmixing model, and our cut-off point for selecting data representative of the young population.

363

364 **Figure 7: Single crystal fusion ages (circles = K-feldspar, squares = biotite) shown with the age distribution**

365 **of the two populations identified by the unmixing model (curves) and the 55 ka cut-off for selecting**

366 **analyses belonging to the youngest population (dashed vertical line). Grey symbols are data excluded**

367 **from the unmixing analyses to allow an approximation of Gaussian distribution for the populations. Filled**

368 **symbols represent data assigned to the young population. Open symbols represent data contaminated**

369 **with excess ^{40}Ar and thus yield ages older than the eruption. Circles = K-feldspar, squares = biotite. Black**

370 **vertical line is the weighted average $\pm 1\sigma$ of the young population ($n=13$). Error bars on individual**

371 **analyses are 1σ .**

372 A further assessment of this age was carried out by plotting an isochron of the data assigned to the young

373 population, giving an age of 50 ± 3 ka, a $^{40}\text{Ar}/^{36}\text{Ar}$ intercept of 297 ± 2 , and an MSWD of 0.5. Figure 5 (lower

374 panel) compares this isochron to the full single crystal fusion data set. This isochron age is indistinguishable

375 from both the weighted average age and the youngest population derived by the unmixing model. Visual

376 inspection of the single crystal fusion isochron plots in Figure 5 shows that the data thought to belong to

the young population form a trend that is qualitatively different from the other analyses, as would be expected when comparing an excess ^{40}Ar -free population with data that are contaminated with excess ^{40}Ar .

5. Discussion and implications

Our preferred estimate of the eruption age is the statistically robust weighted mean (47.4 ± 1.5 ka). It is consistent with a number of previously published ages for the Rotoiti eruption (Berryman, 1993, 1993; Buhay et al., 1992; Charlier et al., 2003; Danišík et al., 2012; Lian and Shane, 2000; Molloy et al., 2009; Nilsson et al., 2011; Santos et al., 2001; Shane et al., 2006; Shane and Sandiford, 2003), but is significantly younger than Wilson et al.'s (2007) age. The latter (61.0 ± 1.4 ka) is based on extrapolation between a K-Ar age for an underlying lava flow and a $^{40}\text{Ar}/^{39}\text{Ar}$ age for an overlying obsidian lava flow (58.5 ± 1.1 ka) that bracket the Rotoehu ash on Mayor Island. Regardless of accuracy of Wilson et al.'s age extrapolation to the Rotoehu ash, the $^{40}\text{Ar}/^{39}\text{Ar}$ age of the overlying lava flow should be younger than that of the Rotoiti eruption; this is not observed for our new eruption age and this discrepancy warrants discussion.

In addition to the overlying lava age, Wilson et al (2007) also report $^{40}\text{Ar}/^{39}\text{Ar}$ ages from stepped heating experiments carried out on multi-grain aliquots of biotite and plagioclase separated from the Rotoiti Pumice, fused lithic clasts similar to the sample analysed in this study, and from the Earthquake Flat Pumice. While some of these ages clearly reflect contamination with excess or inherited ^{40}Ar , others are comparable to Wilson et al.'s proposed eruption age. However, almost half of these ages overlap with our proposed eruption age at 2 standard deviations. Furthermore, as previously noted by Danišík et al. (2012), Wilson et al state that initial stepped heating experiments on biotites from fused lithics yielded younger isochron ages of 47 and 55 ka, but that these were discarded as they were at odds with the bracketing lava ages.

It seems the main discrepancy between our proposed age and that of Wilson et al (2007) concerns the ages of the overlying Mayor Island lava, which was determined on obsidian from the basal carapace. Either this obsidian age is too old or our K-feldspar and biotite ages are too young. To investigate if the discrepancy between our Rotoiti eruption age and Wilson et al's (2007) overlying lava flow age can be explained by

402 differences in assumed fluence monitor age, we recalculated both Mayor Island and Rotoiti eruption ages
 403 according to different monitor ages.

404 Wilson et al (2007) used Taylor Creek sanidine (TCs) as their neutron fluence, with an assumed age of 27.87
 405 Ma (Calvert and Lanphere, 2006), while we used ACs with an age of 1.1851 Ma (Rivera et al., 2013).

406 Published ages for TCs range from 27.87 – 28.62 ka (Duffield and Dalrymple, 1990; Karner and Renne, 1998;
 407 Kuiper et al., 2008; Renne et al., 2010; Sarna-Wojcicki et al., 2000), while recent published ACs ages range
 408 from 1.180 ± 0.0025 Ma (Coble et al., 2011) to 1.2056 ± 0.0019 Ma (Renne et al., 2011). Recalculating the
 409 Mayor Island obsidian flow using a TCs age of 28.62 Ma increases the obsidian age from 58.5 ka to 60.1 ka.
 410 Recalculating our 47.4 ka Rotoiti eruption age using ACs ages of 1.180 Ma and 1.2056 Ma gives ages of 47.2
 411 ka and 48.2 ka respectively. Our eruption age remains significantly younger than Wilson et al's age for the
 412 overlying lava and this discrepancy cannot be explained by differences in fluence monitor age.

413 Young apparent $^{40}\text{Ar}/^{39}\text{Ar}$ ages may result from loss of $^{40}\text{Ar}^*$ during reheating or alteration or by over-
 414 correction for atmospheric ^{40}Ar by an apparent excess of ^{36}Ar . Loss of radiogenic $^{40}\text{Ar}^*$ during reheating is
 415 not thought to be an issue for our samples as these volcanic rocks have remained at the surface of the
 416 earth since they were erupted and so have not experienced subsequent heating events. While alteration
 417 may be an issue for a minority of analyses, our K-feldspar crystals were fresh with a glassy appearance and
 418 were often optically clear and euhedral while the biotite crystals appeared fresh and unaltered. Apparent
 419 excesses of ^{36}Ar may occur due to isobaric interferences in the mass spectrometer from ($^{12}\text{C}_3$) and ($^1\text{H}^{35}\text{Cl}$).
 420 We do not think this is likely as the Noblesse is able to partially resolve ^{36}Ar from ($^{12}\text{C}_3$) and mass 35 was
 421 measured for each analysis to monitor Cl contamination, but never yielded analyses greater than blank
 422 values. If a fractionated Ar-isotope component enriched in ^{36}Ar were incorporated homogeneously into the
 423 crystals, this would result in younger individual apparent ages, but not affect the isochron ages and be
 424 detectable on isotope correlation diagrams. Inhomogeneous incorporation of excess ^{36}Ar may not be
 425 detectable, but this fractionated component would also have to reside in the crystal lattice and be released
 426 at high-temperatures to reproduce the stepped heating data, which seems unlikely. Furthermore, excess
 427 ^{36}Ar has not been documented in crystalline materials before.

428 Whilst obsidian has been successfully used to produce geologically meaningful $^{40}\text{Ar}/^{39}\text{Ar}$ ages (Flude et al.,
429 2010; Morgan et al., 2009; Vogel et al., 2006), it is known to be problematic for reasons that are only just
430 starting to become clear, and it is at least qualitatively possible that these poorly-understood processes can
431 result in over-estimation of $^{40}\text{Ar}/^{39}\text{Ar}$ age spectra and isochron ages. Brown et al. (2009) and Morgan et al.
432 (2009) suggested that the Ar-isotope composition of obsidians in Ethiopia had been affected by kinetic
433 isotope fractionation of atmospheric gas either prior to or during absorption, while Flude et al. (in prep)
434 concluded that kinetic isotope fractionation during magmatic degassing produced heterogeneously
435 distributed excess ^{40}Ar due to preferential loss of ^{36}Ar during degassing. As already discussed, when
436 distributed heterogeneously, excess ^{40}Ar may be difficult to detect via age spectra and isotope correlation
437 diagrams (Kuiper, 2002; Sherlock and Arnaud, 1999), and this may be exacerbated when step-heating
438 aliquots of crushed obsidian which may mix small-scale isotope reservoirs and destroy any naturally
439 occurring isotope profiles that might be detected by stepped-heating of a single fragment (i.e. the
440 laboratory diffusion dimension is less than the natural diffusion dimension). Furthermore, if kinetic isotopic
441 fractionation were to take place during stepped heating of obsidian in the laboratory we would expect ^{36}Ar
442 to be released faster than ^{40}Ar , resulting in relative depression of $^{40}\text{Ar}/^{36}\text{Ar}$ values in the earliest heating
443 steps and elevation in the later heating steps. Isochrons from such data may give apparent ages that are
444 too high with $^{40}\text{Ar}/^{36}\text{Ar}$ intercepts that are too low, thus obscuring the presence of any excess ^{40}Ar and
445 yielding an incorrect but seemingly robust apparent $^{40}\text{Ar}/^{39}\text{Ar}$ age.

446 We are unable to identify a mechanism that could result in our proposed eruption age being under-
447 estimated by ~10-15 kyrs, but it is possible that Wilson et al's (2007) obsidian age is an over-estimate. We
448 also note that our proposed eruption age is within error of many other age estimates for the Rotoiti
449 eruption, is consistent with palaeoenvironmental interpretations (Shane and Sandiford, 2003), and that
450 there are now three radio-isotope techniques (^{14}C , U-Th-He, $^{40}\text{Ar}/^{39}\text{Ar}$) that have yielded consistent
451 eruption ages ~ 45-47 ka. As previously discussed by Danišík et al. (2012), adopting a younger age for the
452 Rotoiti eruption suggests that the TVZ has been much more active than previously realised. Revision

453 increases silicic magma production rates for the Okataina caldera complex from $2.5 \text{ km}^3 \text{ ka}^{-1}$ (Wilson et al.,
454 1995) to $3.8 \text{ km}^3 \text{ ka}^{-1}$ and magma eruption rates of the TVZ are revised to $\sim 17 \text{ km}^3 \text{ kyr}^{-1}$.

455 **5. Conclusions**

456 Vapour phase crystallisation of K-feldspar and biotite in miarolytic cavities of glass-bearing granitoid clasts
457 entrained in the eruption of the Rotoiti ignimbrite provide high-K phases suitable for $^{40}\text{Ar}/^{39}\text{Ar}$ dating of this
458 young, difficult to date eruption. Stepped-heating Ar-isotope analyses on single crystals indicate that excess
459 ^{40}Ar is present in fluid and / or magmatic inclusions present in some of the crystals and is released at low
460 temperatures. This excess ^{40}Ar component is variable and not present in every crystal and so isotope
461 correlation diagrams using single crystal fusion data represent mixing between three components of ^{40}Ar
462 (radiogenic, atmospheric and excess) and do not provide accurate trapped Ar compositions or $^{40}\text{Ar}/^{39}\text{Ar}$
463 ages. An isochron of the stepped heating data is dominated by the moderate-high temperature heating
464 steps and gives an upper limit of the eruption age of $54 \pm 3 \text{ ka}$.

465 The eruption age can be further refined by treating the single-crystal fusion data as a mixed population and
466 assuming that the youngest cohesive age population represents the eruption age. A population unmixing
467 model was used to identify a young population, free from excess ^{40}Ar contamination. This population gave a
468 statistically valid weighted mean eruption age of $47.4 \pm 1.5 \text{ ka}$ which is indistinguishable from recent (U-
469 Th)/He and ^{14}C age determinations by Danišik et al. (2012) and from various other published age
470 determinations based on marine and lake sedimentation rates. However, our new age is significantly
471 younger than the $^{40}\text{Ar}/^{39}\text{Ar}$ age for an obsidian lava flow overlying the Rotoehu ash on Mayor Island,
472 presented by Wilson et al. (2007) and this discrepancy may be explained by kinetic fractionation of Ar-
473 isotopes in obsidian both in nature and the laboratory.

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