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1 **Melt Inclusions in Zircon: A Window to Understanding the**
2 **Structure and Evolution of the magmatic system beneath the**
3 **Laguna del Maule Volcanic Field**

4
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22
23 **Abstract**

24 Explosive silicic eruptions pose a significant threat to society, yet the development and
25 destabilization of the underlying silicic magmatic systems are still controversial. Zircons provide
26 simultaneous information on the trace element composition and age of silicic magmatic systems,
27 while melt inclusions in quartz and plagioclase yield important constraints on their volatile
28 content as well as magma storage depth. Melt inclusions in zircons (MIZs) combine these data

29 from a single mineral grain, recording the age, storage depth, temperature, and composition of
30 magmas, and thus provide unique constraints on the structure and evolution of silicic magmatic
31 systems. We studied MIZs from the Laguna del Maule (LdM) volcanic field in the southern Andes
32 that is among the most active Pleistocene-Holocene rhyolitic volcanic centers worldwide and a
33 potentially hazardous system displaying inflation rates in excess of 25 cm/yr. The host zircon ages
34 suggest that the LdM MIZ record extends to ~30 kyr before eruption, in contrast to the melt
35 inclusions in LdM plagioclase and quartz crystals that formed only decades to centuries before
36 eruption. The major element compositions of MIZs are minimally affected by post-entrapment
37 crystallization, and agree well with the LdM rhyolitic whole rock data. The MIZs record long-term
38 differences in zircon-saturated melt composition between two eruptive units (rdm: Rhyolite of
39 the Laguna del Maule vs. rle: Rhyolite of Los Espejos). The more evolved major element
40 composition of rle MIZs than rdm MIZs, suggests a long-term deeper connection of the rdm
41 crystal mush to a more primitive magma body than that of the rle. The evidence of slow H
42 diffusion observed in MIZs suggest that their H₂O contents are not significantly affected by
43 diffusion of H through the host zircon. The magma storage pressures of 1.1 to 2.8 kbars recorded
44 by the H₂O contents of rdm and rle MIZs are consistent with the optimal emplacement window
45 (2.0 ± 0.5 kbar) of silicic magma reservoir growth, storage, and eruptibility based on
46 thermomechanical modeling (Huber et al. 2019).

47 **1. Introduction**

48 Silicic magmatic systems can generate explosive eruptions of moderate to large sizes (<1
49 to $>10^3$ km³), posing significant risks to local communities and potentially causing substantial
50 disruptions to global climate patterns that can adversely affect human societies and natural
51 ecosystems. Shallow silicic magmas are thought to reside in the crust in the form of a crystal
52 mush comprising less than 50% of melt, making it too viscous to erupt in bulk (Hildreth 2004).
53 The process by which magma reservoirs develop and expand to significant sizes in the shallow
54 crust over thousands of years, as well as the factors that cause destabilization, unrest, and
55 eruption, is a topic of debate (Mahood 1990; Bachmann and Bergantz 2004; Bindeman and
56 Simakin 2014; Wolff et al. 2015). The emerging model of trans-crustal magmatic systems suggests
57 that sub-volcanic magma storage and differentiation occurs within multiple mushy magma
58 reservoirs distributed vertically throughout the crust (Cashman et al. 2017).

59 Zircon has the unique ability to provide simultaneous information on the trace element
60 composition and age within a single crystal domain by in situ microanalytical techniques (e.g.,
61 Claiborne et al. 2010; Reid et al. 2011). The examination of zircon ages and compositions in silicic
62 systems has revealed a variety of processes, such as long-term magma accumulation (10^3 – 10^4
63 years), the merging of magmas with differing compositions, and the remobilization of near-
64 solidus silicic magma (e.g., Bindeman et al. 2008; Wilson and Charlier 2009; Charlier and Wilson
65 2010; Barker et al. 2014; Chamberlain et al. 2014; Wotzlaw et al. 2015; Reid and Vazquez 2017).
66 Zircon has also provided constraints on the duration of mobile and eruptible magma storage
67 prior to eruption, although conflicting observations have been made based on trace element
68 diffusion profiles in zircon that suggest eruptible magmas are a transient feature in a
69 predominantly cool, crystalline, and largely subsolidus crystal mush (Cooper and Kent 2014;
70 Rubin et al. 2017; Szymanowski et al. 2017), while Ti-in-zircon temperatures suggest storage of
71 eruptible magma for a 10^3 – 10^4 year time scale (Barboni et al. 2016).

72 Eruptible rhyolite can be extracted via gravitational compaction and hindered settling
73 (Bachmann and Bergantz 2004), while injections of hotter primitive magma catalyze this process
74 by thermally rejuvenating the crystal-rich magma or remelting the silicic crust and cumulate
75 (Mahood 1990; Bachmann and Bergantz 2004; Bindeman and Simakin 2014; Wolff et al. 2015).

76 Volatiles such as CO₂ and H₂O play an important role, as they can transfer heat from a degassing
77 primitive magma to the overlying crystal mush (e.g., Bachmann and Bergantz 2006), promote
78 melt migration through a crystal mush (e.g., Huber and Parmigiani 2018), cause second boiling,
79 inflation of magma reservoir, and explosive behavior (Blundy and Cashman 2008). Melt inclusions
80 in minerals such as quartz and plagioclase provide important constraints on the volatile content
81 of the primitive and more evolved magma, as well as their storage depth (Wallace et al. 1999;
82 Blundy and Cashman 2005; Wallace 2005).

83 We present major element and H₂O contents of melt inclusions in zircon (MIZs) and the
84 trace element composition and ²³⁰Th-²³⁸U ages of the host zircons erupted in the rhyolitic LdM
85 volcanic field. Values of d¹⁸O are also reported for MIZs and host zircons. LdM volcanic field is
86 among the most active Pleistocene-Holocene rhyolitic volcanic centers worldwide and a
87 potentially hazardous system showing inflation rates >25 cm/yr (Singer et al. 2014a). MIZs can
88 record volatile saturation pressure (H₂O-CO₂ in MIZ), temperature (Ti-in-zircon thermometer),
89 composition (MIZ major and trace element), and time (²³⁰Th-²³⁸U ages) that provide a unique set
90 of constraints on the understanding of the structure and evolution of silicic magmatic systems
91 (e.g., Thomas et al. 2003). Using our data, we distinguish and evaluate the effect of post-
92 entrapment modification versus primary magmatic processes on the MIZ composition through
93 crystallization and diffusive exchange. We then use our data to examine the structure and storage
94 conditions of magma reservoirs at LdM through time.

95

96 **2. Geological setting**

97 The Laguna del Maule volcanic field is located in the Southern Volcanic Zone (SVZ) of
98 central Chile, 30 km behind the active volcanic front (Fig. 1). The volcanism at LdM has been
99 dominantly silicic and concentrated within the central lake basin since the most recent glacial
100 retreat, which is estimated to have occurred locally at c. 23 to 19 ka based on ⁴⁰Ar/³⁹Ar dates of
101 unglaciated lava flows (Singer et al. 2000; Andersen et al. 2017). Both effusive and explosive
102 eruptions at LdM yielded rhyolites that contain less than 10 vol.% phenocrysts of plagioclase,
103 biotite, and magnetite ±quartz ±amphibole ±zircon. The 20 km³ plinian Rhyolite of Laguna del
104 Maule (rdm), thought to have erupted from a vent beneath the modern lake (Fierstein 2018), is

105 the earliest known post-glacial rhyolite. The subsequent rhyolite eruptions, each less than 3 km³
106 in volume, occurred most frequently during an early post-glacial (EPG) period from 22.5 to 19 ka,
107 and during the middle to late Holocene. Rhyodacite and andesite eruptions also occurred
108 throughout post-glacial times, but comprise a smaller cumulative volume than the rhyolites and
109 were concentrated in the western LdM basin, away from the locus of rhyolite volcanism. Based
110 on these observed spatial relations, Hildreth et al. (2010) proposed that a massive silicic magma
111 reservoir is present below LdM, obstructing the rise of mafic magma.

112 This hypothesis is increasingly supported by geological, geochronological, and geophysical
113 studies, which suggest that the shallow magma system is still active at present with ongoing
114 average inflation of ~20 cm/year since 2007 (up to 29 cm/year) (Feigl et al. 2014; Le Mevel et al.
115 2015; Le Mevel et al. 2016; Andersen et al. 2017; Miller et al. 2017; Andersen et al. 2018; Cordell
116 et al. 2018; Fierstein 2018; Singer et al. 2018; Wespestad et al. 2019; Le Mével et al. 2021). Both
117 surface- and teleseismic-tomography have shown the presence of a crystal-rich reservoir with
118 450 to 500 km³ of partial melt at a depth of 2-12 km beneath the northwest portion of the lake
119 at LdM (Wespestad et al. 2019; Bai et al. 2020). Magnetotelluric observation suggests the
120 presence of a deeper partially molten reservoir that extends beyond 15 km depth (Cordell et al.
121 2018; Cordell et al. 2019).

122 Plagioclase trace element compositions as well as plagioclase and quartz melt inclusions
123 have provided constraints on magma extraction processes and magma storage conditions that
124 have not been available from whole rock data (Andersen et al. 2018; Klug et al. 2020). Trace
125 element diffusion modeling of LdM plagioclase suggests a short time scale (decades to centuries)
126 between extraction of crystal-poor rhyolite from crystal mush and its eruption (Andersen et al.
127 2018). Melt inclusions in plagioclase and quartz revealed shallowing magma storage depth with
128 increasing degree of melt differentiation, with the latter being more evolved and recording lower
129 H₂O contents/shallower storage depth (Klug et al. 2020). Based on these observations, Klug et al.
130 (2020) argued that crystal-poor rhyolite went through decompression-driven fractional
131 crystallization as it ascended from ~14 km to ~4 km shortly before eruption.

132 Zircon petrochronology records up to 160 kyr of rhyolitic magma production in the crystal
133 mush reservoir of the LdM (Andersen et al. 2019). The significant age difference between

134 plagioclase and quartz (decades to centuries) compared to zircon has been attributed to
135 extraction of rhyolite from a crystal mush entraining smaller zircons preferentially over larger
136 crystals of major phases (Claiborne et al. 2010; Stelten and Cooper 2012; Andersen et al. 2019).
137 Based on the Ti-in-zircon thermometry as well as modeling of zircon crystallization rates,
138 contemporaneous existence of hot zones and regions of cold storage within the mush reservoir
139 has been hypothesized (Andersen et al. 2019).

140

141 **3. Samples and Methods**

142 **3.1 Samples**

143 The sample that is the main focus of this study is from the 20 km³ plinian rdm unit (22.5
144 to 19 ka) that comprises ash and pumice lapilli (up to 4 cm in diameter) from quickly cooled
145 tephra within well-defined stratigraphic sections (Klug et al. 2020). We report data from an
146 additional sample of the Los Espejos rhyolite (rle) unit, which erupted at 19.0 ± 0.4 ka subsequent
147 to rdm (Andersen et al. 2017).

148

149 **3.2 Mount preparation**

150 A ~2 kg pumice sample of the rdm unit was crushed and sieved into ≥ 250 μm and < 250
151 μm size fractions. Approximately 1000 zircon grains were separated from the < 250 μm fraction
152 using conventional techniques including Wilfley-type shaking table, Frantz isodynamic magnetic
153 separator, and heavy liquid separation. The zircon grains were then handpicked, cast in epoxy
154 grain mounts, and polished. At least two grains each of UWZ-1 zircon (Valley et al. 2024) and
155 UWQ-1 quartz (Kelly et al. 2007) standards were also cast in the same mount. The relief between
156 the grains and adjacent epoxy was minimized to < 1 μm and grains were placed in the central 8
157 mm radius region of the mount to ensure good spot-to-spot reproducibility (Kita et al. 2009;
158 Peres et al. 2013). In addition to the epoxy mount, we also studied a mount with LdM zircons that
159 was prepared and analyzed by Andersen et al. (2019) who pressed the zircon grains into soft
160 indium and analyzed euhedral crystal faces for trace elements and ^{230}Th - ^{238}U isotope ratios. The
161 indium mount was then polished to expose the crystal interiors which were also analyzed for

162 trace elements and ^{230}Th - ^{238}U isotope ratios by Andersen et al. (2019). The MIZs exposed in these
163 zircons were studied here, which are all from the rle unit.

164

165 **3.3 Imaging of zircons/MIZs**

166 Zircons were imaged by reflected light, backscattered electrons (BSE), and
167 cathodoluminescence (CL) using a Hitachi S-3400N Scanning Electron Microscope (SEM) and
168 Gatan Chroma CL system at the University of Wisconsin–Madison. For both the epoxy and indium
169 mounts, we focused only on zircons that have MIZs. The crystal sizes range from 57 to 174 μm
170 on the long axis and 26 to 88 μm on the short axis with aspect ratios of 1 to 3.3 (Figs. 2 and S1).
171 Zircon morphologies range from anhedral to euhedral and prismatic and all the crystals are clear
172 and colorless. In CL, the zircons are characterized by sector and oscillatory zoning. Around some
173 melt/mineral inclusions, the host zircon is characterized by undulating CL pattern and/or bright
174 CL (Fig. S1).

175 All zircon grains were imaged by BSE to look for MIZs exposed at the grain surface. A
176 potential issue to this approach is that some of the 3D context of the MIZ and host zircon is lost
177 from the polishing process of exposing the MIZ. This limits certain characterization of the MIZs
178 such as their volume and dimensions, their spatial distribution within the host zircon, as well as
179 the potential presence of vapor bubbles and crystals (e.g., Sobolev and Kostyuk 1975; Roedder
180 1984; Bodnar and Student 2006; Rose-Koga et al. 2021) in the MIZs that may have been polished
181 away. Despite the loss of certain 3D context, it is highly unlikely that the MIZs were
182 embayment/melt channel that were in contact with the surrounding melt based on the clearly
183 distinct H_2O content and major element composition of the MIZs compared to those of the
184 surrounding melt (i.e., matrix glass) (sections 4.2 and 4.3) indicating lack of communication
185 between the MIZs and the surrounding melt.

186 Qualitative analyses of major elements of MIZs were done by an Oxford AZtecOne energy-
187 dispersive X-ray spectroscopy (EDS) system with acceleration voltage and beam current of 15 kV
188 and 1 nA, respectively. We carefully selected MIZs that are glassy and homogeneous. We also
189 avoided MIZs that are visibly intersected by cracks in the host zircon. The nineteen MIZs identified
190 in 17 rdm zircon grains range from 8 to 25 μm on the long axis and 5 to 14 μm on the short axis

191 with aspect ratios of 1.1 to 5.3 (Figs. 2 and S1). Six MIZs found in the rle zircons range from 5 to
192 43 μm on the long axis and 3 to 5 μm on the short axis with aspect ratios of 1.1 to 8.7 (Figs. 2 and
193 S1). On the exposed surface, all 25 MIZs are glassy and 20 are completely homogeneous while 5
194 of them are mostly homogeneous except small microcrystals of titanomagnetite and pyroxene
195 (not shown). Nineteen of the MIZs are circular to oval in shape, while six are elongated to
196 irregularly shaped. Four out of 17 rdm zircon grains have matrix glass adhered onto them.

197

198 **3.4 EPMA of MIZs**

199 Chemical composition of the MIZs was measured with a CAMECA SXFive Field Emission
200 Electron Probe Microanalyzer (FE-EPMA) at the Department of Geoscience at the University of
201 Wisconsin–Madison. The sample mounts were coated with a 20 nm carbon layer after being
202 cleaned with distilled water and ethanol. Analyses were conducted with an accelerating voltage
203 of 15 kV, a beam current of 1 nA, and a beam diameter of 2 or 3 μm . The low beam current was
204 selected to minimize beam induced element migration during the EPMA measurements. Major
205 elements (Na, Al, Si, Mg, K, Ca) were measured for 200 s and quantified using Mean Atomic
206 Number (MAN) background regression (Donovan et al. 2016). Oxygen and the remaining minor
207 elements (P, Fe, Mn, Ti, Zr) were quantified using off-peak background regression and measured
208 for 60 s on peak and 30 s on each high and low background position. An exponential background
209 regression was used for analysis of O. Time-dependent intensity corrections were applied for Na,
210 K, Si, and O. Analysis of hydrous haplogranite glass (6.6 wt% H_2O ; Morgan and London 2005) was
211 used to evaluate accuracy of the analytical routine. Many of the zircon MIZs had diameter < 5
212 μm . This resulted in secondary fluorescence of Zr from the surrounding zircon matrix. Monte-
213 Carlo simulation of electron-specimen interactions using PENEPMASIM was used to constrain the
214 extent of secondary fluorescence for various inclusion dimensions and beam diameters. Addition
215 of Zr into the analysis routine was used to monitor the effects of secondary fluorescence on
216 individual measurements; any measurements with >1 wt% ZrO_2 were interpreted as affected by
217 secondary fluorescence and discarded from consideration. For MIZ analyses with < 1 wt.% ZrO_2 ,
218 the compositions were corrected to be ZrO_2 -free, assuming essentially all Zr signal was from host
219 zircon.

220

221 **3.5 SIMS**

222 **3.5.1 Zircon $\delta^{18}\text{O}$; MIZ $\delta^{18}\text{O}$ and H_2O**

223 Zircon oxygen isotope ratios as well as MIZ oxygen isotope ratios and H_2O contents were
224 measured using the CAMECA IMS-1280 secondary ion mass spectrometer (SIMS) at the WiscSIMS
225 laboratory at the University of Wisconsin–Madison. The zircon epoxy mount was gold-coated
226 after being cleaned with distilled water and ethanol and kept in a vacuum oven at 60°C for 24
227 hours. Zircon analyses were made following the methods described previously (Kita et al. 2009;
228 Valley and Kita 2009; Wang et al. 2014). A primary $^{133}\text{Cs}^+$ ion beam was focused to 10 μm diameter
229 with an intensity of 1.7 to 1.8 nA, to generate $\sim 3 \times 10^9$ counts per second (cps) of secondary $^{16}\text{O}^-$
230 ions. The multicollecion (MC) Faraday cup (FC) detectors were used to simultaneously measure
231 $^{16}\text{O}^-$, $^{18}\text{O}^-$, and $^{16}\text{O}^1\text{H}^-$ signals with feedback resistors of 10^{10} , 10^{11} , and $10^{11} \Omega$, respectively.
232 Individual zircon analyses lasted approximately 3.5 min including sputtering of the gold coated
233 surface (10 s), automatic centering of the secondary ion beam in the field aperture (60 s), and 40
234 cycles of 4 second integrations of oxygen ion measurements. Analysis pits were $\sim 2 \mu\text{m}$ deep. For
235 the MIZ analysis, the primary Cs^+ ion beam was focused to 3 μm diameter with an intensity of 25
236 pA, to generate $\sim 3.5 \times 10^7$ counts per second (cps) of secondary $^{16}\text{O}^-$ ions. Each MIZ analyses lasted
237 approximately 4 min including sputtering of the gold coated surface (30 s), automatic centering
238 of the secondary ion beam in the field aperture (60 s), and 20 cycles of 8 second integrations of
239 oxygen ion measurements. The $^{16}\text{O}^-$ and $^{18}\text{O}^-$, and $^{16}\text{O}^1\text{H}^-$ signals were measured simultaneously
240 in two FCs ($^{16}\text{O}^-$ and $^{16}\text{O}^1\text{H}^-$, both with feedback resistors of $10^{11} \Omega$) and one electron-multiplier
241 (EM) for $^{18}\text{O}^-$ ($\sim 7 \times 10^4$ cps). Hydride interferences at mass 18 were resolved at mass resolving
242 power (MRP at 10% peak height) of 2,200, and MRP of 5,000 was used for mass 17 to resolve
243 $^{16}\text{O}^1\text{H}^-$ from $^{17}\text{O}^-$. A liquid N_2 trap was used to maintain vacuum in the sample chamber $\leq 5 \times 10^{-9}$
244 mbar to reduce hydrogen background. Four analyses of UWZ-1 zircon standard were made at the
245 beginning of the session and after every 10 unknowns. The bracketing sets of eight analyses of
246 UWZ-1 ($\delta^{18}\text{O} = 4.98 \text{‰}$ VSMOW) were used to monitor instrumental bias for zircon standard and
247 the spot-to-spot reproducibility for individual brackets, which ranged between 0.17 and 0.21 ‰
248 (2SD) for the zircon analyses and 0.51 to 0.75 ‰ (2SD) for the MIZ analyses.

249 For H₂O contents of MIZs, calibration was made between the measured ¹⁶O¹H⁻/¹⁶O⁻ and
250 H₂O content using rhyolitic glass standards with known H₂O concentrations (Newman et al. 1986;
251 Singer et al. 2014b; Klug et al. 2020). The major element compositions of these rhyolitic glass
252 standards encompass those observed in the MIZ (Fig. S2). For the February 2022 session, we
253 obtained a linear regression line between ¹⁶O¹H⁻/¹⁶O⁻ versus H₂O wt.% (0.33 to 3.51 wt.% H₂O
254 rhyolitic glasses; Newman et al. (1986), Klug et al. (2020)) (Fig. S3a, Table S2). The majority of MIZ
255 H₂O contents obtained during this session were beyond the calibration range (> 3.5 wt.%). A
256 subsequent session in June 2022 was conducted, in which we measured higher H₂O content
257 standards (0 to 6.09 wt.% H₂O rhyolitic glasses; Singer et al. (2014b)). We obtained a polynomial
258 regression line between ¹⁶O¹H⁻/¹⁶O⁻ versus H₂O wt.% (Fig. S3b, Tables S3). The H₂O contents of
259 MIZs that were analyzed during both February 2022 and June 2022 sessions that agree to within
260 10% on average (Fig. S3c). For both sessions, the background levels of ¹⁶O¹H⁻/¹⁶O⁻ were
261 determined by multiple analyses of the UWZ-1 zircon grains, which were subtracted from the
262 ¹⁶O¹H⁻/¹⁶O⁻ of the melt inclusion analyses before converting them to H₂O wt.%. The background
263 corrections were typically smaller than 10% of measured ¹⁶O¹H⁻/¹⁶O⁻ values. To correct for MIZ
264 δ¹⁸O instrumental mass fractionation, anhydrous glass standards with known δ¹⁸O (Jochum et al.
265 2006) were analyzed that have a range of SiO₂ from 51.4 to 75.6 wt.% (Tables S2 and S3). The
266 δ¹⁸O bias was estimated relative to zircon (bias*) as a function of the SiO₂ content of the glass
267 standards. The δ¹⁸O of individual MIZs were corrected for the bias based on the bias estimated
268 from bracketing zircon standard analyses and the relative bias (bias*) of each MIZ that is
269 calculated using the SiO₂ content (EPMA data). The effect of H₂O on the MIZ δ¹⁸O instrumental
270 mass fractionation was evaluated using some of the aforementioned hydrous rhyolitic glass
271 standards as well as hydrous basaltic glass standards that had previously been analyzed for δ¹⁸O
272 (Newman et al. 1988; Eiler et al. 2000). This showed that the instrumental biases of the hydrous
273 glasses agree well with those of the anhydrous glasses such that the effect of H₂O on the MIZ
274 δ¹⁸O instrumental mass fractionation is minimal.

275

276 3.5.2 Zircon trace elements

277 Zircons were analyzed for 26 trace elements (Al, P, Ca, Sc, Ti, Fe, Y, Nb, La, Ce, Pr, Nd, Sm,
278 Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, Th, U) using the CAMECA IMS-1280 secondary ion mass
279 spectrometer (SIMS) at the WiscSIMS laboratory at the University of Wisconsin–Madison.
280 Analyses used a $^{16}\text{O}^-$ primary beam at a current of 5.4 nA and a total impact energy of 23 kV (–13
281 kV at the ion source and +10 kV on the sample surface). Analytical pits were $\sim 13\ \mu\text{m}$ in diameter.
282 The mass spectrometer was operated at a nominal mass resolving power ($\text{MRP} = M/\Delta M$) of
283 14,000, which allows for separation of $^{45}\text{Sc}^+$ and $^{93}\text{Nb}^+$ from interferences with $^{90}\text{Zr}^{++}$ and $^{92}\text{ZrH}^+$,
284 respectively (e.g., Grimes et al. 2015; Coble et al. 2018; Blum et al. 2023). No energy offset was
285 applied because most molecular interferences, such as REE oxides on REE, were fully resolved.
286 Each analysis included a 30 second pre-sputter, centering of the secondary beam within the field
287 aperture, and five cycles of counting from low to high mass by magnetic peak-jumping on axial
288 mono-collector (mostly EM except for major element Si and Zr peaks on FC). Normalized count
289 rates (normalizing species ^{28}Si) are converted to trace element concentrations based on element
290 specific relative sensitivity factors (RSFs). RSFs were determined for the primary reference
291 material, NIST610 (Pearce et al. 1997) with correction factors based on multiple zircon reference
292 materials to account for matrix mismatch between glass and zircon, similar to those in previous
293 studies (Page et al. 2007; Bouvier et al. 2012; Kitajima et al. 2012). Zircon reference materials
294 analyzed in this study are 91500 (Wiedenbeck et al. 2004; Coble et al. 2018), MAD-559 (Coble et
295 al. 2018), and GZ7 (Nasdala et al. 2018). For elements (Al, Ca, Sc, and Fe) that do not have
296 homogeneous or well characterized published values in the reference material suite, no
297 correction factor is applied (Wiedenbeck et al. 2004; Coble et al. 2018). Additional analytical
298 details will be published elsewhere.

299

300 **3.5.3 Zircon ^{230}Th - ^{238}U**

301 To prepare the zircon epoxy grain mount for SIMS U-Th analyses, the mount was cleaned
302 with a 10% EDTA (ethylenediaminetetraacetic acid) wash, thoroughly rinsed with DI water, then
303 given a quick $\sim 30\text{s}$ rinse in 1M HCl to remove surface contamination before being dried at 50°C
304 in a vacuum oven for 30 minutes. The sample surface was coated with $\sim 10\text{-}20\ \text{nm}$ of gold for
305 conductivity before being loaded in the instrument sample lock chamber.

306 Zircon U-Th analyses were conducted on the SHRIMP-RG (reverse geometry) ion
307 microprobe in the co-operated Stanford and U. S. Geological Survey SUMAC facility at Stanford
308 University. Analytical procedure and data reduction follows methods developed by Williams
309 (1997) and Ireland and Williams (2003). An O_2^- primary beam with accelerating voltage of 10 kV
310 was used to sputter secondary ions from the sample surface with a ~ 19 nA primary beam current
311 focused to ~ 42 μm . Prior to analysis, spots were presputtered for 60 seconds remove gold coating
312 and surface contamination from the analysis area, and the primary and secondary beams were
313 auto-tuned to maximize transmission. Seven masses were measured, including $^{90}Zr_2^{16}O$, $^{238}U^+$,
314 $^{232}Th^{12}C^+$, $^{230}Th^{16}O^+$, background measured 0.050 AMU above the $^{230}Th^{16}O^+$ peak, $^{232}Th^{16}O^+$, and
315 $^{238}U^{16}O^+$. An energy slit set to 1 mm width was employed to reduce interferences. Data were
316 collected over 8 scans per spot, for a total run time of 33 minutes, collected by magnet peak-
317 jumping on an EPT discrete-dynode electron multiplier. Mass resolution ($M/\Delta M$) was set to
318 ~ 8000 for all masses, sufficient to resolve any interfering molecular species.

319 Zircon U concentration data were standardized against the well-characterized MAD-559
320 (3940 ppm U; Coble et al. 2018) and MAD-1 zircon standards (Barth and Wooden 2010) measured
321 from a separate mount that was co-loaded in the analysis chamber. $(^{238}U)/(^{232}Th)$ and
322 $(^{230}Th)/(^{232}Th)$ ratios were calculated using $\lambda_{238} = 1.55125 \times 10^{-7} \text{ ka}^{-1}$ (Jaffey et al. 1971), $\lambda_{232} =$
323 $4.9475 \times 10^{-8} \text{ ka}^{-1}$ (Steiger and Jäger 1977), $\lambda_{230} = 0.0091705 \text{ ka}^{-1}$ (Cheng et al. 2013). The
324 $(^{238}U)/(^{232}Th)$ was also corrected for instrument mass fractionation using early-erupted Bishop
325 Tuff ($767.1 \pm 0.9 \text{ ka}$, Crowley et al. 2007), which is relatively high-U (1000-4000 ppm) and old
326 enough that the U-Th is in secular equilibrium. For analyses measured in this session $(^{230}Th)/(^{238}U)$
327 $= 0.8461 \pm 0.0069$ (1σ , $n = 9$, MSWD = 2.2), which is the RSF that was applied to the unknowns.
328 Data was reduced using the Microsoft Excel add-in programs Squid2.51 and Isoplot3.764 of Ken
329 Ludwig (Ludwig 2001; 2003).

330

331 4. Results

332 4.1 ^{230}Th - ^{238}U ages of the LdM zircons

333 We determined the ^{230}Th - ^{238}U ages of 11 rdm zircons, ranging from 18.7 ka to secular
334 equilibrium ($>350 \text{ ka}$) (Fig. 3). Out of the 11 rdm zircon grains that were dated, four of them

335 (hereafter referred to as younger rdm zircons) have non-secular equilibrium ages that range from
336 18.7 to 47.0 ka, falling within the ^{230}Th - ^{238}U ages (18.1 to 78.8 ka) previously determined for the
337 zircons from the same unit (Andersen et al. 2019). The youngest zircon age is $18.7^{+5.0}_{-4.7}$ (1SD) ka,
338 which agrees well with the eruption age of the rdm unit (19-23 ka based on field relationships).
339 The remaining seven rdm zircon grains are in secular equilibrium indicating unresolvable ages
340 that are >350 ka (hereafter older rdm zircons). The six rdm zircon grains that could not be dated
341 (hereafter no age (NA) rdm zircons) either due to the size or SHRIMP beam overlapping epoxy
342 are not included in further discussion given the difficulty in putting them in context of other data
343 without their ^{230}Th - ^{238}U ages. For the rle zircons, the previously determined ^{230}Th - ^{238}U ages range
344 from 14.9 to 80.8 ka, and those with MIZs found in this study are 19.7 to 48.3 ka (Andersen et al.
345 2019). No MIZ was found in the rle zircon that is in secular equilibrium.

346

347 **4.2 Major elements**

348 The major element composition of the younger rdm MIZs are all rhyolitic (75.1 to 76.6
349 wt.%) and relatively homogeneous (Fig. 4). Their composition agrees well with the tight array
350 defined by the whole rock data of the post-glacial silicic units (Hildreth et al. 2010; Andersen et
351 al. 2017). Their composition is less evolved compared to the rdm whole rock data (Hildreth et al.
352 2010; Andersen et al. 2017) and the rdm matrix glasses (Contreras et al. 2022) (Fig. S4). The
353 younger rdm MIZs agree well with the most evolved side of the compositional range defined by
354 the rdm plagioclase melt inclusions, which show significant range in SiO_2 (71 to 76 wt.%) (Fig. S4).
355 However, the younger rdm MIZs are less evolved compared to the rdm quartz melt inclusions
356 (Klug et al. 2020) (Fig. S4).

357 In contrast to the younger rdm MIZs, the major element composition of older rdm MIZs
358 are rhyodacitic to rhyolitic, significantly more heterogeneous, and for the most part do not agree
359 well with those of the rdm whole rock/melt inclusions nor with those of the post-glacial silicic
360 units (Andersen et al. 2017) (Fig. 4). The post-glacial whole rock data form a tight array of
361 chemical data, while the whole rock composition of older units (> 25 ka) is more scattered (Fig.
362 S5). Some of the older rdm MIZs agree with the composition of these older units (Hildreth et al.
363 2010). However, many of the older rdm MIZs are anomalous (e.g., those with high K_2O of > 6

364 wt.%) even compared to the whole rock composition of the older eruption units. While there
365 may be a tendency for CL pattern of zircons surrounding older rdm MIZs to have more complex
366 patterns (Fig. S1), clear correlation between MIZ composition and surrounding zircon CL pattern
367 were not observed.

368 Similar to the younger rdm MIZs, the major element composition of the rle MIZs agree
369 well with the trend defined by the whole rock data of the post-glacial silicic units (Andersen et al.
370 2017) (Fig. 4). The three less evolved rle MIZs are compositionally similar to the rle whole rock
371 data (Hildreth et al. 2010; Andersen et al. 2017) and rle matrix glasses (Contreras et al. 2022),
372 while the other 3 rle MIZs are more evolved ($\text{SiO}_2 = 77$ to 78 wt.%) (Figs. 4 and S6). The more
373 evolved rle MIZs are compositionally similar to the rle plagioclase melt inclusions, most of which
374 are similarly evolved ($\text{SiO}_2 = 76$ to 78 wt.% for 11 out of 12 plagioclase melt inclusions) (Klug et
375 al. 2020) (Fig. S6).

376

377 **4.3 H₂O contents**

378 The H₂O contents of the younger rdm MIZs span 4.1 to 5.7 wt.%, and they agree well with
379 those of the rdm plagioclase melt inclusions (Klug et al. 2020) (Fig. 5). In contrast, the H₂O
380 contents of older rdm MIZs are significantly scattered (2.1 to 6.6 wt.%) compared to the range
381 observed in the rdm plagioclase melt inclusions, reaching similarly low H₂O contents as some
382 quartz melt inclusions (Klug et al. 2020) (Fig. 5). A measurement of the matrix glass adhered onto
383 an undated rdm zircon (zircon f4) yielded a distinctly lower H₂O content of 0.05 wt.% in
384 comparison to MIZs. The H₂O contents of the rle MIZs (4.3 to 6.2 wt.%) are comparable to the
385 younger rdm MIZs, although extending to slightly higher H₂O contents. These H₂O contents are
386 comparable with those in the rle plagioclase melt inclusions (5.4 to 5.8 wt.%) (Klug et al. 2020).

387

388 **4.4 Oxygen isotope ratios**

389 Oxygen isotope ratios of the rdm zircons are homogeneous regardless of age (i.e.,
390 younger or older rdm) ($\delta^{18}\text{O} = 5.76 \pm 0.32$ ‰, 2SD) (Fig. 6a). The $\delta^{18}\text{O}$ values of younger rdm MIZs
391 are also homogeneous ($\delta^{18}\text{O} = 8.22 \pm 0.80$ ‰, 2SD), while that of older rdm MIZs is highly variable
392 ($\delta^{18}\text{O} = 4.1$ to 8.9 ‰) (Fig. 6a). The oxygen isotopic fractionation between the glass in younger

393 rdm MIZ and host-zircon is relatively constant ($\Delta^{18}\text{O}_{\text{MIZ-Zrn}} = 2.59 \pm 1.01 \text{ ‰}$, 2SD) (Fig. 6b), and
394 within uncertainty with the equilibrium zircon-melt oxygen isotopic fractionation factor (Lackey
395 et al. 2008). The equilibrium fractionation between zircon and melt is nearly constant at
396 magmatic temperatures (Lackey et al. 2008; Grimes et al. 2011; Bucholz et al. 2017). In contrast,
397 oxygen isotopic fractionation between the older rdm MIZ and host-zircon is highly variable
398 ($\Delta^{18}\text{O}_{\text{MIZ-Zrn}} = -1.52$ to 3.22 ‰) (Fig. 6b), and some do not preserve equilibrated values from
399 magmatic conditions. The oxygen isotopic composition of the rle MIZs/zircons were not
400 determined, due to the lack of suitable oxygen isotope standard grain in the indium mount.

401

402 **4.5 Ti-in-zircon thermometry**

403 Ti-in-zircon temperatures were calculated using the calibration of Ferry and Watson
404 (2007), which requires the TiO_2 activity (a_{TiO_2}), SiO_2 activity (a_{SiO_2}) and pressure. Following the
405 previous study on LdM zircons of Andersen et al. (2019), we first used the a_{TiO_2} of 0.72 obtained
406 based on magnetite-ilmenite equilibrium (Ghiorso and Evans 2008) and an a_{SiO_2} of 1 based on the
407 presence of quartz in the LdM rhyolites (Andersen et al. 2017). The effect of pressure was not
408 taken into account, but such effect is relatively small ($\sim 50^\circ\text{C}/10 \text{ kbar}$). Ti-in-zircon temperatures
409 calculated based on these a_{TiO_2} and a_{SiO_2} values along with the measured Ti content in zircons
410 span 708 to 839°C (younger rdm = 708 to 792°C , older rdm = 722 to 839°C , rle = 724 to 796°C).
411 These are comparable to the Ti-in-zircon temperatures previously determined for LdM zircons
412 (Andersen et al. 2019) as well as the temperature range of LdM rhyolites estimated based on the
413 Fe-Ti oxide thermometer (Andersen et al. 2017).

414

415 **4.6 Zircon trace elements**

416 The trace element composition (e.g., U, Hf, Ti, REE contents) of the younger rdm zircons
417 agree well with those that were previously observed for rdm zircons (Andersen et al. 2019) (Fig.
418 7). While it is somewhat unexpected given the anomalous major element composition of older
419 rdm MIZs (Fig. 4), the trace element composition of older rdm zircons compares well with other
420 rdm zircons (Fig. 7a). The Ti content of younger rdm zircons range from 5 to 12 ppm, and
421 correlates negatively with their Hf content that ranges from 8,500–10,700 ppm (Fig. S7). The U

422 content of the younger rdm zircons range from 353 to 1,688 ppm, which tends to correlate with
423 the bright and dark CL regions, respectively. The trace element composition of the rle zircons
424 with MIZs ($U_{Zrn} = 266\text{--}557$ ppm, $Ti_{Zrn} = 6\text{--}12$ ppm, $Hf_{Zrn} = 8,100\text{--}10,700$ ppm) are representative
425 of those of the larger rle zircon data set, except for the most U-rich and -depleted zircons
426 (Andersen et al. 2019). The melt in equilibrium with the zircons calculated using the zircon-melt
427 REE partition coefficients (Sano et al. 2002) are consistent with the whole rock data for the LdM
428 post-glacial units (Andersen et al. 2017) (Fig. S8).

429

430 **5. Discussion**

431 **5.1 Post-entrapment modification of MIZs**

432 Subsequent to entrapment in the host crystal, melt inclusions can be modified by
433 processes such as devitrification, crystallization of new zircon, cracking of host zircon and
434 diffusive exchange with the surrounding melt (e.g., Danyushevsky et al. 2002). However, multiple
435 lines of evidence suggest that post-emplacment processes have had minimal effects on many
436 of the MIZs from rdm and rle units, and that many of the MIZs retain major element, oxygen
437 isotopic composition, and water contents of the entrapped magmas. Post-entrapment
438 crystallization (PEC) (e.g., Kress and Ghiorso 2004) of zircon during cooling is minimal for MIZs
439 given the small concentration of Zr in the melt. For example, LdM whole rocks have a maximum
440 Zr content of 265 ppm (Hildreth et al. 2010), which limits the maximum amount of PEC of zircon
441 to < 0.05 wt.% in a MIZ, assuming Zr content of 500,000 ppm in zircon and that all Zr in the melt
442 is converted to zircon. The effect of PEC of other minerals on the composition of the MIZs in this
443 study is difficult to constrain as we did not conduct heating experiments. However, the younger
444 rdm as well as the rle MIZs in this study have minimal to no textural evidence by SEM of PEC
445 phases given their homogeneous nature (Figs. 2 and S1). Further, the agreement between the
446 major element composition of younger rdm and rle MIZs ($^{230}\text{Th}\text{--}^{238}\text{U}$ age of host zircon < 60 ka)
447 to those of whole rock data of the post-glacial silicic units (Andersen et al. 2017), as well as those
448 of plagioclase and quartz melt inclusions from the same unit (Klug et al. 2020), suggests that PEC
449 did not have a substantial effect on the younger rdm and rle MIZ compositions (Fig. 4). In contrast,
450 the major element composition of most older rdm MIZs ($^{230}\text{Th}\text{--}^{238}\text{U}$ age of host zircon in secular

451 equilibrium) significantly deviate from those of whole rock, and plagioclase and quartz melt
452 inclusions, which could be due to the effect of PEC. Nevertheless, the most notable difference in
453 major element composition between younger rdm and older rdm MIZs would require a
454 substantial amount of PEC (e.g., K₂O of 4.4 wt.% in younger rdm MIZ vs. 6.5 wt.% in some older
455 rdm MIZs require ~33 wt.% crystallization of quartz) if the original melts were of the same
456 composition. The lack of substantial PEC minerals in SEM images of the older rdm MIZs does not
457 support such large amount of PEC (Figs. 2 and S1). Together with the old age (>350 ka) of the
458 older rdm MIZs, a more likely explanation is that they formed from a parental melt that formed
459 under magmatic conditions unrelated to those that produced the younger rdm and rle MIZs and
460 other LdM units.

461 Melt inclusions can record the pre-eruptive volatile contents of magmas. However, after
462 entrapment, volatiles can sometimes diffuse into or out of melt inclusions through the host
463 mineral (e.g., Qin et al. 1992). There are so far no experimental measurements of H diffusion
464 coefficient in zircon under conditions relevant to the LdM zircons (e.g., *f*O₂ conditions). In the
465 LdM MIZs, we observe a negative correlation between the degree of differentiation (SiO₂) and
466 H₂O contents of MIZs (Fig. 5) that is consistent with those observed in plagioclase and quartz melt
467 inclusions. This negative correlation has been interpreted to suggest decompression-driven
468 fractional crystallization and H₂O degassing as the rdm magma ascended from deeper to
469 shallower portion of the LdM reservoir (Klug et al. 2020). The preservation of such negative
470 correlation in the rdm MIZs strongly suggests the retention of MIZ H₂O contents since the time
471 of entrapment, as diffusive exchange would decouple H₂O from SiO₂ in the MIZs. Some older rdm
472 MIZs (>350 ka) are characterized by low H₂O contents for a given SiO₂ (Fig. 5), and may indicate
473 instances of H₂O leakage from these MIZs. With these exceptions aside, we infer that the negative
474 correlation between SiO₂ and H₂O contents to indicate that the MIZs in this study were not
475 significantly impacted from diffusive equilibration of H through the host zircon since the time of
476 entrapment.

477

478 **5.2 Identification of xenocrystic rdm zircons/MIZs (older rdm)**

479 The older rdm zircons that are in secular equilibrium (>350 ka) host MIZs that are
480 anomalous in composition (Fig. 4). Their compositions do not agree with those of the rdm unit
481 nor other whole rock data of the post-glacial silicic units and older units (Hildreth et al. 2010;
482 Andersen et al. 2017). The older rdm MIZs are generally low in FeO and MgO and also show
483 significantly more variable CaO, TiO₂, as well as H₂O contents for a given SiO₂ content compared
484 to the younger rdm and rle MIZs and LdM whole rock data (Figs. 4 and 5). Three older rdm MIZs
485 have significantly higher K₂O content than younger rdm and rle MIZs as well as LdM whole rock
486 (Fig. 4). These high K₂O older rdm MIZs have anomalously low $\delta^{18}\text{O}$ values that are not in isotopic
487 equilibrium with the host zircon (Fig. 6b). While the distinct major element composition could in
488 part be due to post-entrapment crystallization of certain phases, high K₂O contents and
489 anomalously low $\delta^{18}\text{O}$ observed in some MIZs are difficult to explain by such process. Taken
490 together with their secular equilibrium ages (>350 ka), we hypothesize that older rdm
491 zircons/MIZs are xenocrystic in origin and that the MIZs record older exotic melt compositions
492 that formed under magmatic conditions unrelated to those that produced the rdm and rle
493 eruptions. The highly variable H₂O content of older rdm MIZs also supports this hypothesis. Our
494 observation shows the importance of age dating the host zircon in order to avoid xenocrystic
495 zircons that may host MIZs with chemical composition that is irrelevant to the magmatic system
496 of interest. In terms of the origin of the older rdm zircons, they may have originated from deeper
497 granites that are represented by crustal xenoliths found in the pyroclastic flow facies of the rdm
498 unit. These are exceptionally large (up to ~1 m) crustal debris with heterogeneous lithologies that
499 could be Pliocene-Miocene plutonic rocks that housed the magmatic precursor to the more
500 recent LdM system, analogous to those observed in the Risco Bayo-Huemul plutonic complex 20
501 km west of the LdM system (Schaen et al. 2018; Schaen et al. 2021). The other post-glacial units
502 including the rle do not contain such granitoid xenoliths. The rdm unit is exceptional in this regard,
503 which explains the uniquely high abundance of secular equilibrium age zircons in the rdm units
504 compared to other units including the rle unit.

505

506 **5.3 Major element composition and H₂O contents of the younger rdm and rle MIZs:**
507 **Implications for the LdM magmatic system**

508 In contrast to the older rdm zircons and MIZs, the geochemical data of the younger rdm
509 zircons and MIZs are consistent with their formation from the active magmatic system that
510 underlies the LdM. The ^{230}Th - ^{238}U ages of $18.7^{+5.0}_{-4.7}$ to $47.0^{+4.0}_{-3.9}$ (1SD) ka for the younger rdm
511 zircons agrees with the previously determined ^{230}Th - ^{238}U ages (18.1 to 78.8 ka) of the rdm unit
512 zircons (Andersen et al. 2019). All younger rdm MIZs are in oxygen isotopic equilibrium with their
513 host zircon (Fig. 6b). The major element compositions of younger rdm MIZs are akin to those of
514 the whole rock data for the rdm unit as well as other post-glacial LdM units (Hildreth et al. 2010;
515 Andersen et al. 2017), matrix glasses (Contreras et al. 2022), and plagioclase/quartz melt
516 inclusions (Klug et al. 2020) (Figs. 4 and S4). The SiO_2 contents of these younger rdm MIZs are
517 consistent with the predicted SiO_2 content (>70 wt.%) above which the LdM whole rocks become
518 zircon saturated based on their Zr content and zircon saturation models of Watson and Harrison
519 (1983) and Boehnke et al. (2013) (Andersen et al. 2017). In addition, the trace element
520 concentrations (e.g., REE, U, Hf, Ti contents, Eu/Gd) of younger rdm zircons are also within those
521 that were previously observed for rdm zircons (Andersen et al. 2019) (Fig. 7). Following the same
522 reasoning, rle zircon trace element composition and ^{230}Th - ^{238}U ages (Andersen et al. 2019) (Fig.
523 7) and the rle MIZ composition (Figs. 4 and S6) supports the notion of their formation from the
524 magmatic system that underlies the LdM. Hence, the younger rdm and rle zircons in this study
525 formed from melts in a growing crystal mush over a significant part of its 60 kyr history (based
526 on the oldest zircon ages of Andersen et al. (2019)), and the MIZs hosted in these zircons record
527 the compositions and storage depths of the zircon-saturated regions within the crystal mush melt
528 over time. In order to correlate the ^{238}U - ^{230}Th age from the host zircon with the MIZ composition,
529 uncertainties associated with the placement of the age spots relative to the location of the MIZs
530 within the host zircon were considered. We used the CL images of the host zircon (Fig. S1-1) to
531 determine if an age spot can be considered to date the (1) age of the MIZ entrapment (when the
532 age spot is directly in the same CL domain as the MIZ), or should rather be considered to date
533 the (2) minimum or (3) maximum age of the MIZ entrapment (depending on whether the age
534 spot is in a CL domain that is further away from (i.e., min. age) or closer to (i.e., max. age) the
535 zircon core than the MIZ (refer to the caption of Fig. 8 for details)).

536 The younger rdm and rle MIZ compositions record relatively homogeneous crystal mush
537 melt composition during its buildup (Fig. 8) that is consistent with the post-glacial silicic whole
538 rock data (Fig. 4). However, there are compositional differences between the younger rdm and
539 rle MIZs. The younger rdm MIZs are on average less differentiated (e.g., lower SiO₂, higher Al₂O₃
540 and MgO) than the rle MIZs (Fig. 8), and this difference is observed from at least ~30 kyr before
541 eruption until close to the eruption ages of both units (19 to 23 ka) (Fig. 8). Less evolved rdm MIZ
542 compared to rle MIZ is consistent with the hypothesis that the rdm crystal mush was better
543 connected to the deeper mid-crustal plumbing system than the rle crystal mush, as proposed by
544 Klug et al. (2020) based on the less evolved rdm plagioclase melt inclusion with deeper
545 entrapment depths as compared to those of rle. While the plagioclase melt inclusions were
546 entrapped only decades to centuries before eruption (Andersen et al. 2018), MIZs record a
547 persistent difference between rdm and rle going back to ~30 kyr before eruption, suggesting the
548 long-term connection of the rdm crystal mush to deeper depths (higher T and lesser degree of
549 plagioclase/zircon fractionation) than that of the rle.

550 The magma storage pressures recorded by the entrapment pressures of younger rdm
551 MIZs are 1.1 to 2.8 kbars (4.0 to 10.5 km depth) (Fig. 9), based on their H₂O contents, assumed
552 range of CO₂ content of 0 to 570 ppm (based on the plagioclase-hosted melt inclusions from the
553 rdm unit), and the MagmaSat model of Ghiorso and Gualda (2015) implemented in the VesiCal
554 v1.01 software (Iacovino et al. 2021). There is no clear correlation between the storage pressure
555 and the MIZ entrapment age for the younger rdm MIZs (Fig. 9). The magma storage pressures are
556 consistent with those by the silicic plagioclase-hosted melt inclusions from the rdm unit (1.6 to
557 2.4 kbars) (Klug et al. 2020) that formed decades to centuries before the eruption of the rdm unit
558 based on the disequilibrium trace element profiles (Andersen et al. 2018). Similar to the rdm
559 MIZs, the rle MIZs record magma storage pressures of 1.4 to 2.8 kbars (5.3 to 10.4 km depth)
560 (assuming MIZ CO₂ of 25 to 344 ppm based on the plagioclase-hosted melt inclusions from the
561 rle unit) that match well with those recorded by the rle plagioclase melt inclusions (1.7 to 2.2
562 kbars) (Klug et al. 2020). The magma storage pressure recorded by the rle MIZs appears to
563 decrease through time (Fig. 9), but the significance of this trend is unclear given the small number
564 of MIZs. The agreement between the magma storage pressures recorded by the MIZs and the

565 plagioclase-hosted melt inclusions suggests that the storage depths of evolved melts that are
566 zircon- (+plagioclase- ± quartz-) saturated were relatively constant from the time of MIZ
567 entrapment (younger rdm and rle zircon ages of 18.7 to 47.0 ka and 19.7 to 55.8 ka, respectively)
568 until the time of rdm and rle eruption (plagioclase age of decades to centuries before eruption
569 at 19 to 23 ka for rdm and 19 ± 0.4 ka for rle). The magma storage pressures of 1.1 to 2.8 kbars
570 recorded by younger rdm and rle MIZs are consistent with the optimal emplacement window
571 (2.0 ± 0.5 kbar) of silicic magma reservoir growth, storage, and eruptibility based on the
572 thermomechanical model of Huber et al. (2019).

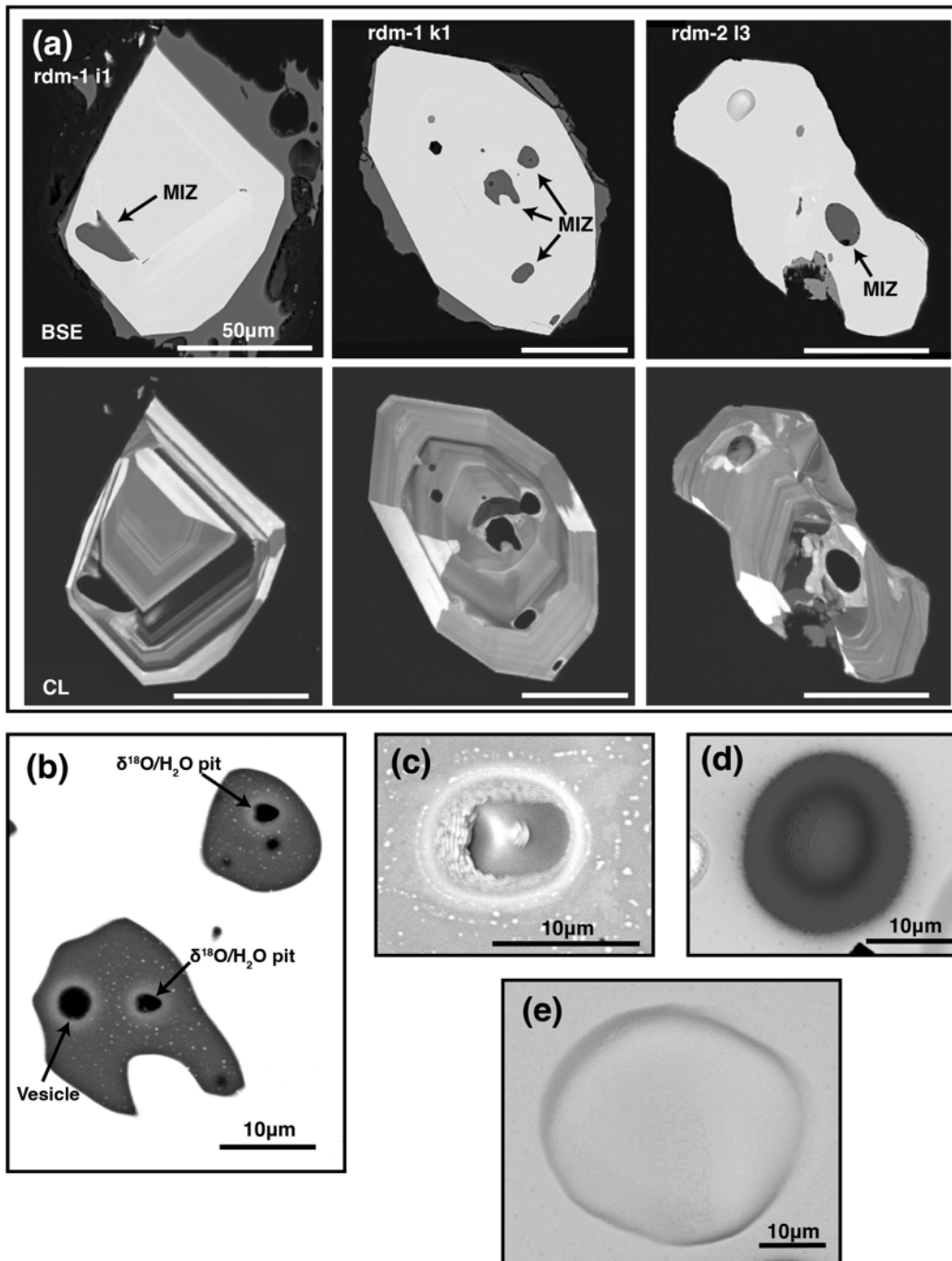
573

574 **5. Conclusion**

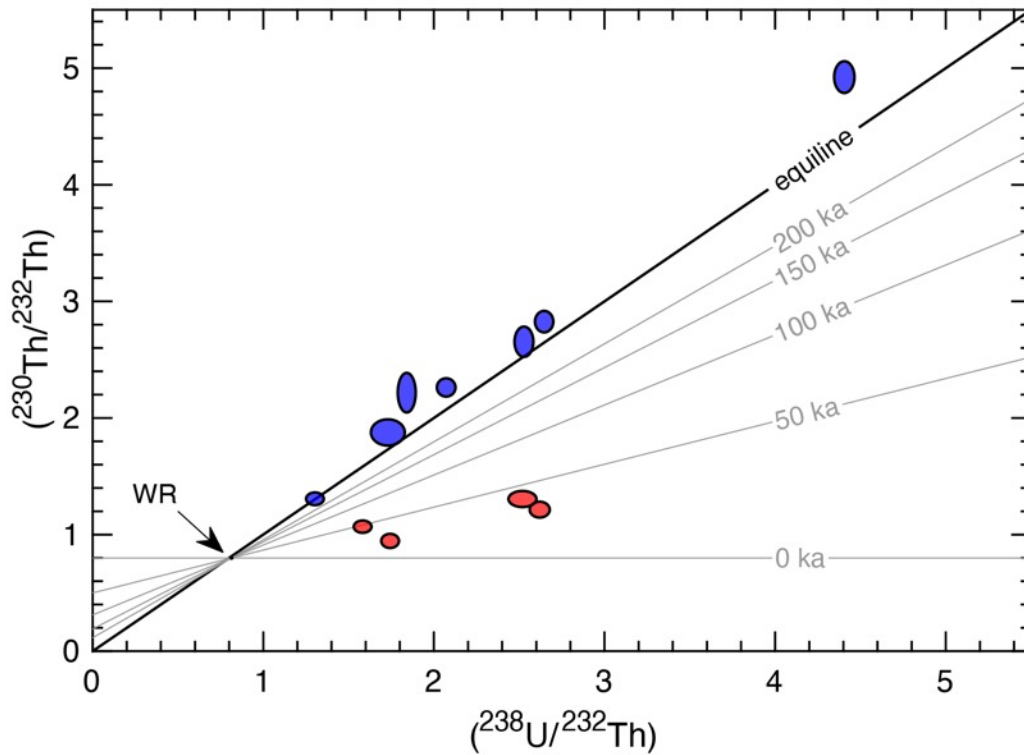
575 The study of MIZs from the Laguna del Maule volcanic field provides unique insights into
576 the structure and evolution of silicic magmatic systems. MIZs extend the record of magma
577 compositions back to ~30 kyr before the eruption, providing important constraints on the age,
578 storage depth, temperature, and composition of magmas. We observe a long-term difference in
579 zircon-saturated melt composition between the rdm and rle eruption units, with the rdm MIZs
580 indicating a less evolved crystal mush than that of the rle. These findings suggest that since
581 ~30 kyr before eruption, the rdm crystal mush was better connected to a deeper and more
582 primitive magma body than the rle crystal mush. The correlation between SiO_2 and H_2O contents
583 observed in the MIZs suggests that the H_2O contents of the MIZs are not significantly affected by
584 diffusion of H through the host zircon. The rdm and rle MIZs record storage depths of 1.1 to 2.8
585 kbars that are consistent with the optimal emplacement window (2.0 ± 0.5 kbar) of silicic magma
586 reservoir growth, storage, and eruptibility based on thermomechanical model of Huber et al.
587 (2019).

588 **6. Acknowledgements**

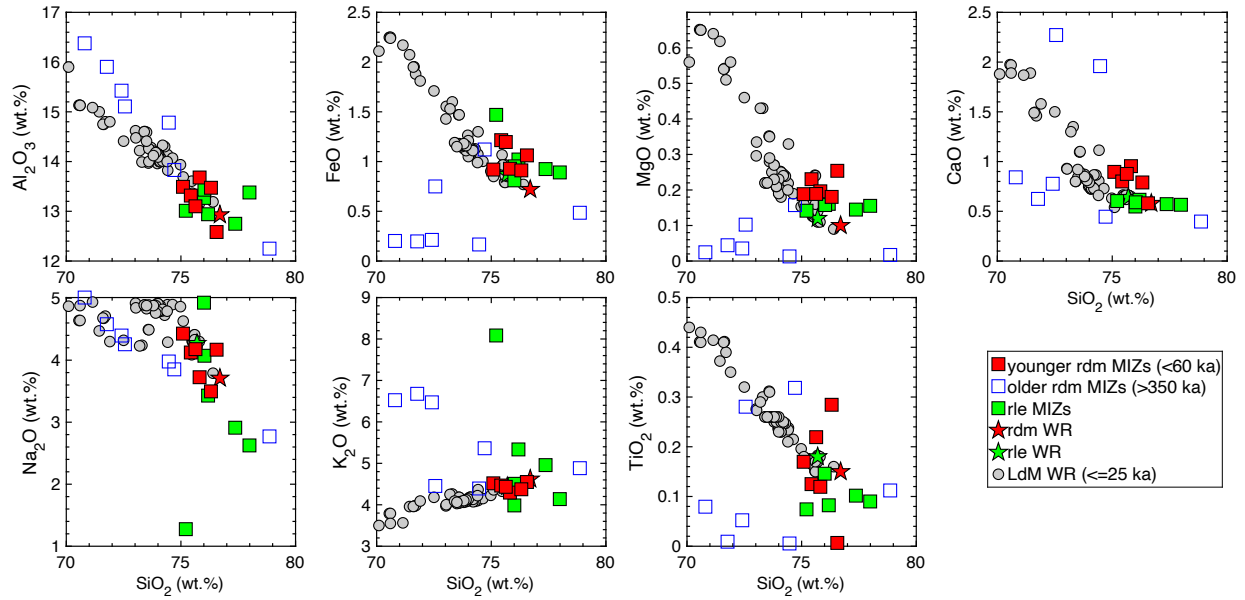
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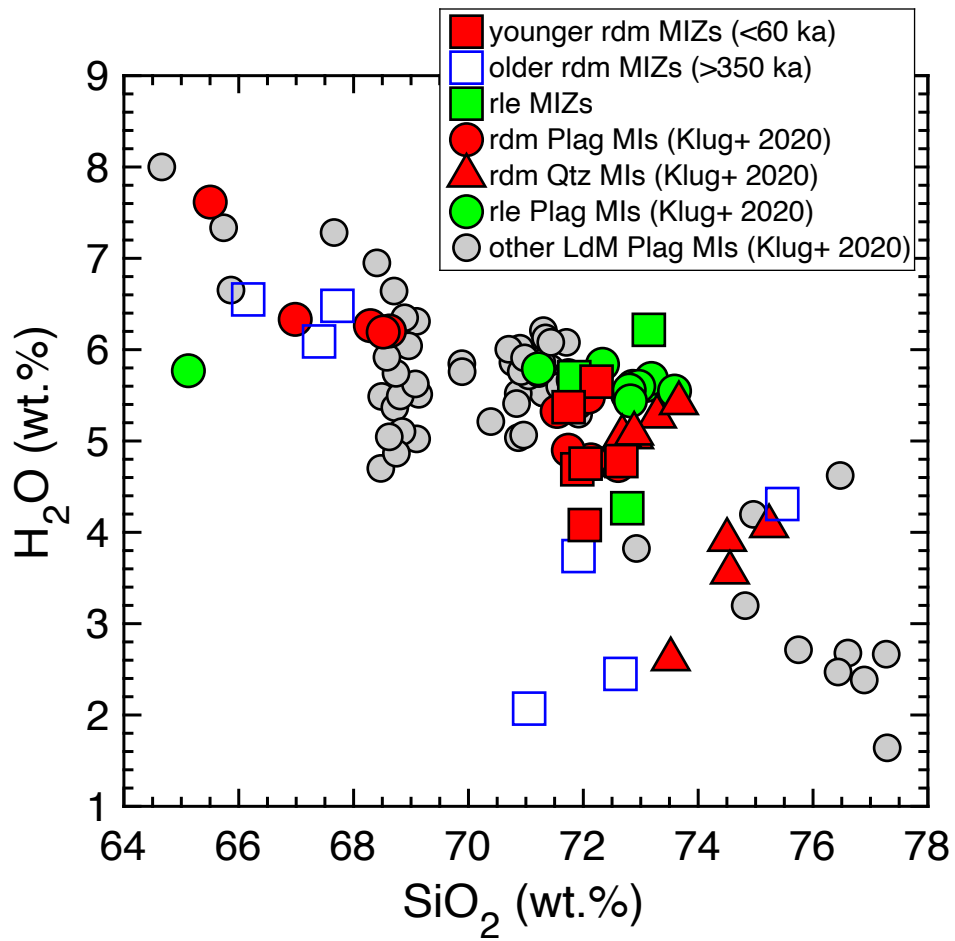
608
 609 Figure 2. (a) BSE and CL images of representative MIZs/host zircons (scale bars = 50 μm). (b) BSE
 610 image of SIMS pits and Cs spatter from the analyses of $\delta^{18}\text{O}/\text{H}_2\text{O}$ of the MIZ (~3 μm diam.). (c)
 611 and (d) BSE images of SIMS pits from the analyses of $\delta^{18}\text{O}$ (~10 μm diam.) and trace element (~13
 612 μm diam.) of the zircons, respectively. (e) BSE image of a SHRIMP pit from the ^{238}U – ^{230}Th age
 613 dating of the zircons (~40 μm diam.).
 614



615
 616 Figure 3. ^{238}U – ^{230}Th isochron diagram for zircons from the rdm unit of the LdM. Each ellipse
 617 represents a SHRIMP-RG analysis of a spot in separate zircon grains. Error ellipses are 1SD. Red
 618 ellipses are analyses on the younger rdm zircons (non-secular equilibrium ages), while the blue
 619 ellipses are analyses of older rdm zircons (secular equilibrium ages). The small black dot
 620 represents the whole rock composition used to calculating the model ages (average of post-
 621 glacial rhyolite whole rock data from Andersen et al. (2017)). The heavy black line represents the
 622 equiline, while the gray lines represent isochrons of ages from 0 to 200 ka. Some older rdm
 623 zircons plot above the equiline, which is likely due to the primary beam overlapping with the
 624 epoxy that causes elevated $^{230}\text{ThO}^+$ background.



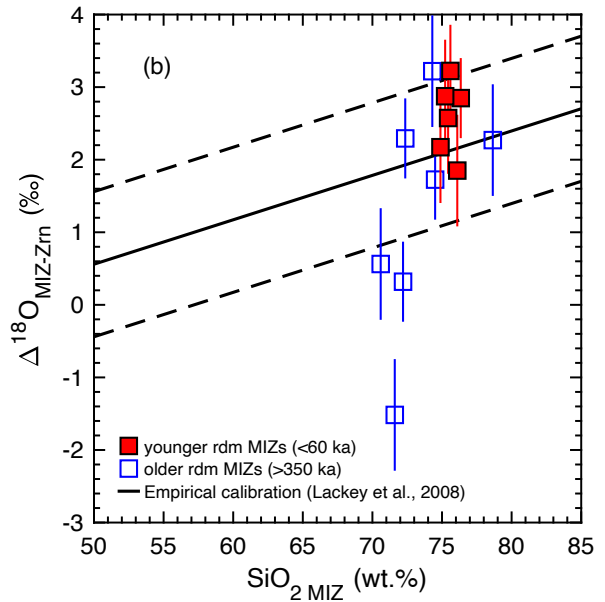
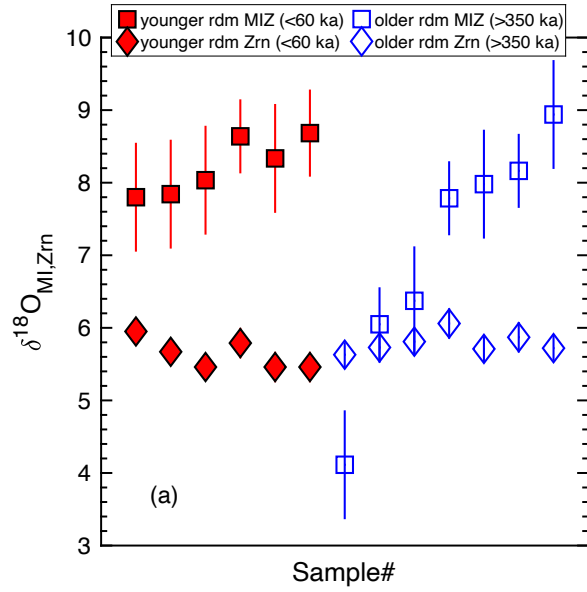
625
 626 Figure 4. Harker diagrams showing the major element composition of the rdm and rle MIZs and
 627 correlated whole rock compositions. Whole rock data of younger units (≤ 25 ka) are from
 628 Andersen et al. (2017), Hildreth et al. (2010), and Contreras et al. (2022). MIZ compositions are
 629 normalized to 100% on anhydrous basis to allow direct comparison with the whole rock data. The
 630 matrix glass, and melt inclusions in plagioclase and quartz, and the whole rock composition of
 631 older units (> 25 ka) are not shown for clarity.



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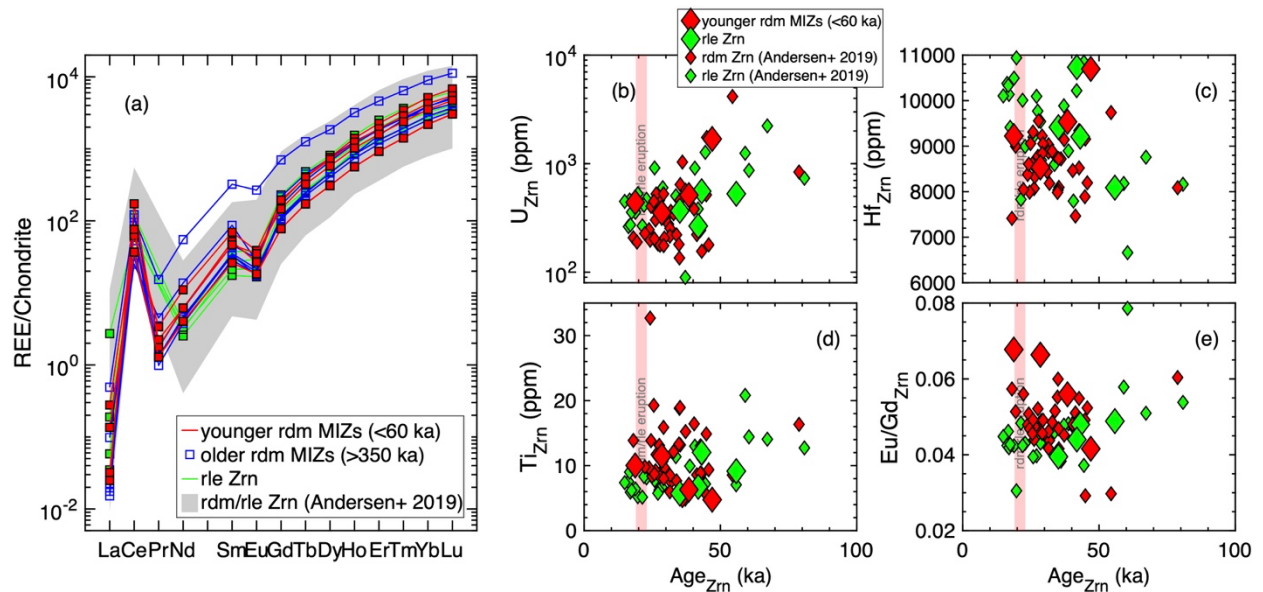
633 Figure 5. H₂O and SiO₂ contents of the rdm and rle MIZs along with plagioclase and quartz melt

634 inclusions (Klug et al. 2020).



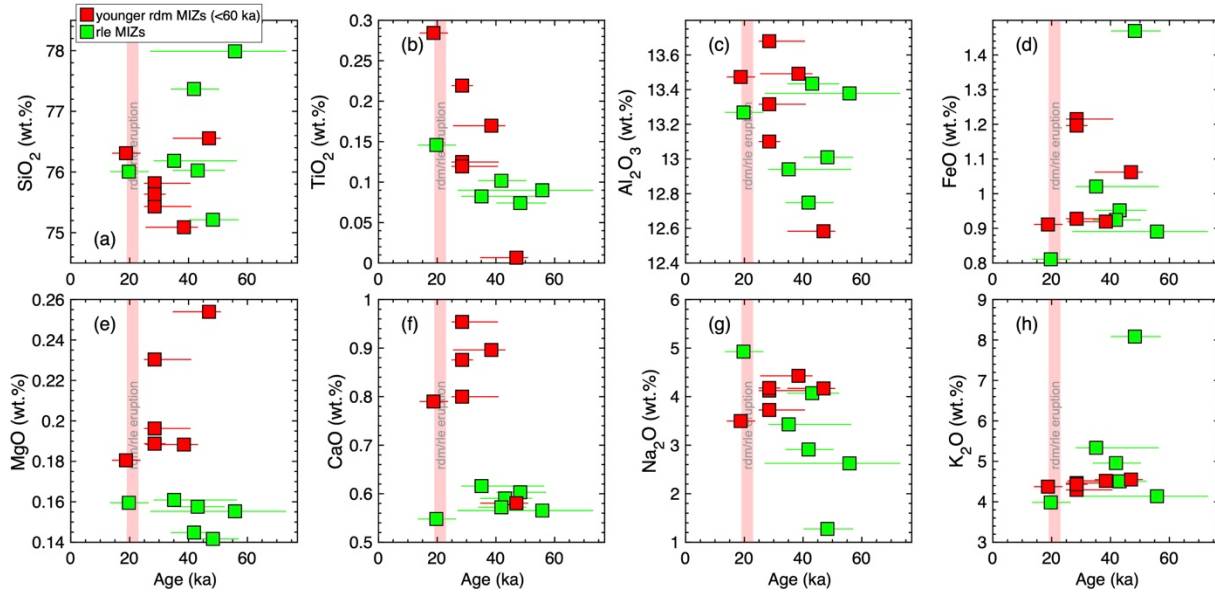
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636 Figure 6. (a) $\delta^{18}\text{O}$ of the MIZ (squares) and zircon host (diamonds). (b) $\Delta^{18}\text{O}_{\text{MIZ-Zrn}}$ vs. SiO_2 content
 637 of the MIZ. In (b), the dashed line shows the predicted melt-zircon equilibrium isotopic
 638 fractionation (Valley et al. 2005; Lackey et al. 2008).



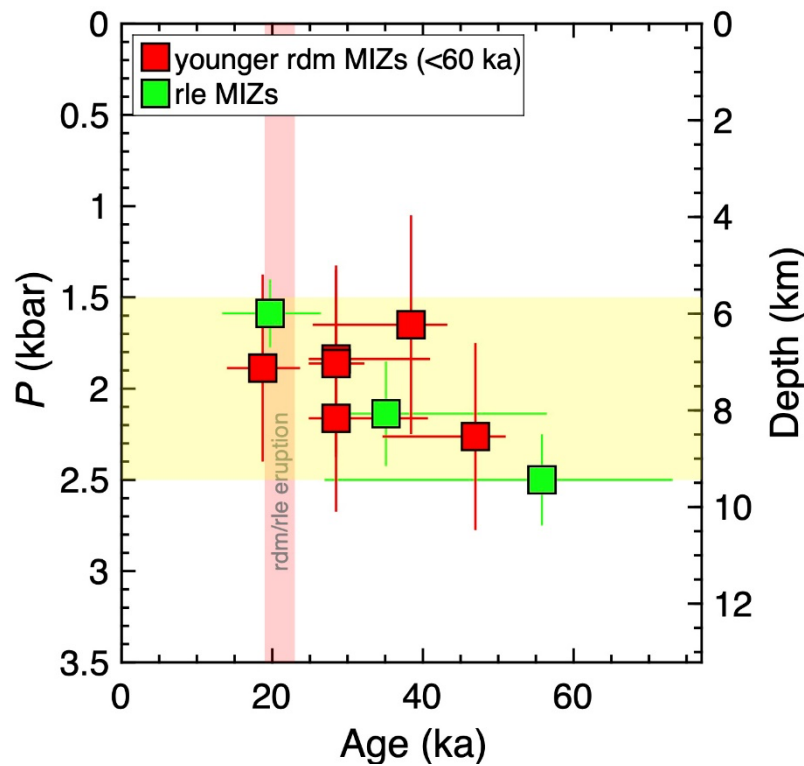
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Figure 7. (a) Chondrite normalized REE pattern and (b) U, (c) Hf, (d) Ti, and (e) Eu/Gd vs. ²³⁸U–²³⁰Th ages of the rdm and rle zircons. In (a) the gray field shows the rdm and rle zircon REE data from Andersen et al. (2019). In (b, c, d, and e), older rdm zircons are not shown given their secular equilibrium ages. The large symbols are from this study, while the small symbols are rdm and rle zircon trace element data from Andersen et al. (2019). The vertical light-red bar shows the eruption age of rdm and rle units (Andersen et al. 2017). Chondrite REE values are from (McDonough and Sun 1995).



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Figure 8. Major element composition of the rdm and rle MIZs vs. their entrapment ages estimated based on the ^{238}U – ^{230}Th age data of the host zircons. The vertical light-red bar shows the eruption age of rdm and rle units (Andersen et al. 2017). As discussed in section 5.3, some ^{238}U – ^{230}Th age spots should be considered to be the minimum (i.e., age spot in CL domain further away from zircon core than that of the MIZ) or maximum (i.e., age spot in CL domain closer to zircon core than that of the MIZ) entrapment ages of the MIZs. In such cases, we estimated the maximum or minimum MIZ entrapment ages based on the mean age difference between the zircon rim and interior ages of the rdm (8.5 kyr) and rle (13.9 kyr) zircons (Andersen et al. 2019). For example, if the age spot is in a CL domain that is closer to the zircon core than the CL domain that the MIZ is in (e.g., rdm-1 i1, Fig. S1-1), the ^{238}U – ^{230}Th age ($47.0^{+4.0}_{-3.9}$ ka) was considered the maximum age of MIZ entrapment and the minimum age was estimated by subtracting the mean age difference between the zircon rim and interior ages of the rdm (8.5 kyr) zircons (Andersen et al. 2019) from the negative uncertainty of the ^{238}U – ^{230}Th age (entrapment age = $47.0^{+4.0}_{-12.4}$ ka).



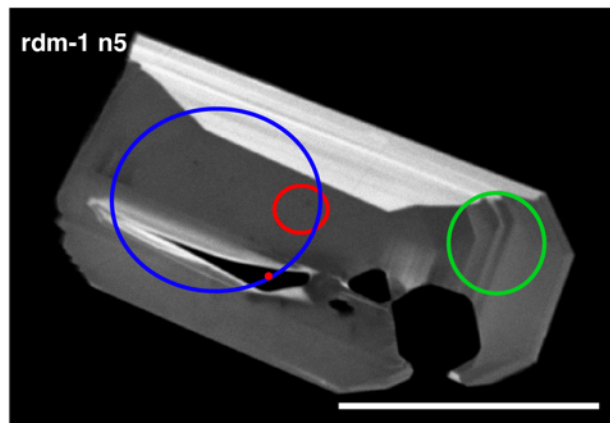
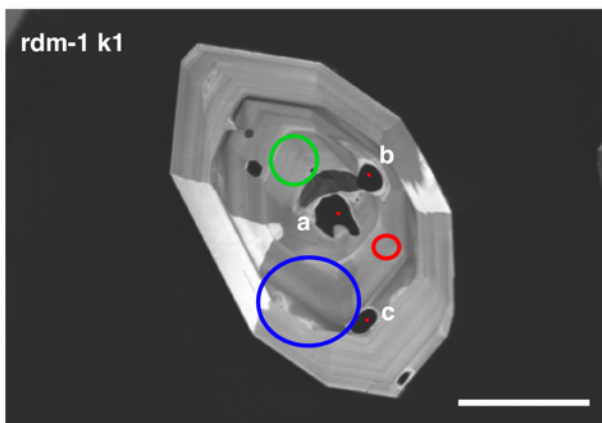
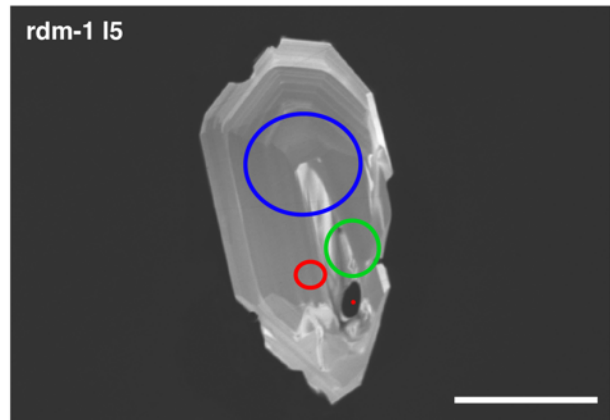
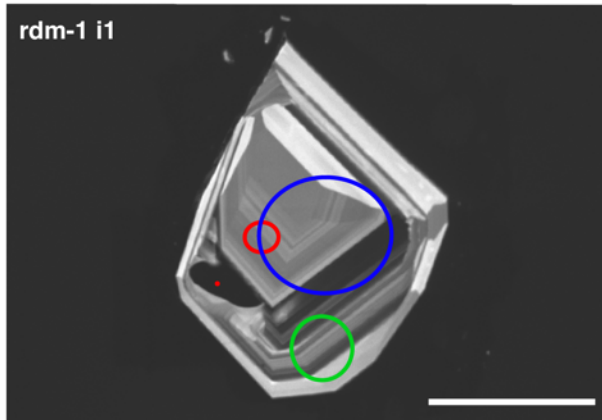
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666 Figure 9. Magma storage pressures recorded by the rdm and rle MIZs vs. their entrapment ages
 667 estimated based on the ^{238}U – ^{230}Th age data of the host zircons. The pressures were calculated
 668 based on the MIZ H_2O contents, ranges of MIZ CO_2 content assumed based on plagioclase-
 669 hosted melt inclusion data (Klug et al. 2020) (0 to 570 ppm and 25 to 344 ppm for rdm and rle
 670 MIZs respectively) and the MagmaSat model of Ghiorso and Gualda (2015) implemented in the
 671 VesiCal v1.01 software (Iacovino et al. 2021). The vertical light-red bar shows the eruption age
 672 of rdm and rle units (Andersen et al. 2017). The horizontal light-yellow bar indicates the optimal
 673 emplacement window (2.0 ± 0.5 kbar) of silicic magma reservoir growth, storage, and
 674 eruptibility based on thermomechanical model of Huber et al. (2019). Depth on the right axis is
 675 calculated with a crustal density of $2,700 \text{ kg/m}^3$. For the description of the uncertainties in the
 676 MIZ entrapment ages, refer to section 5.3 and caption of Fig. 8.

677 **Supplementary figures**

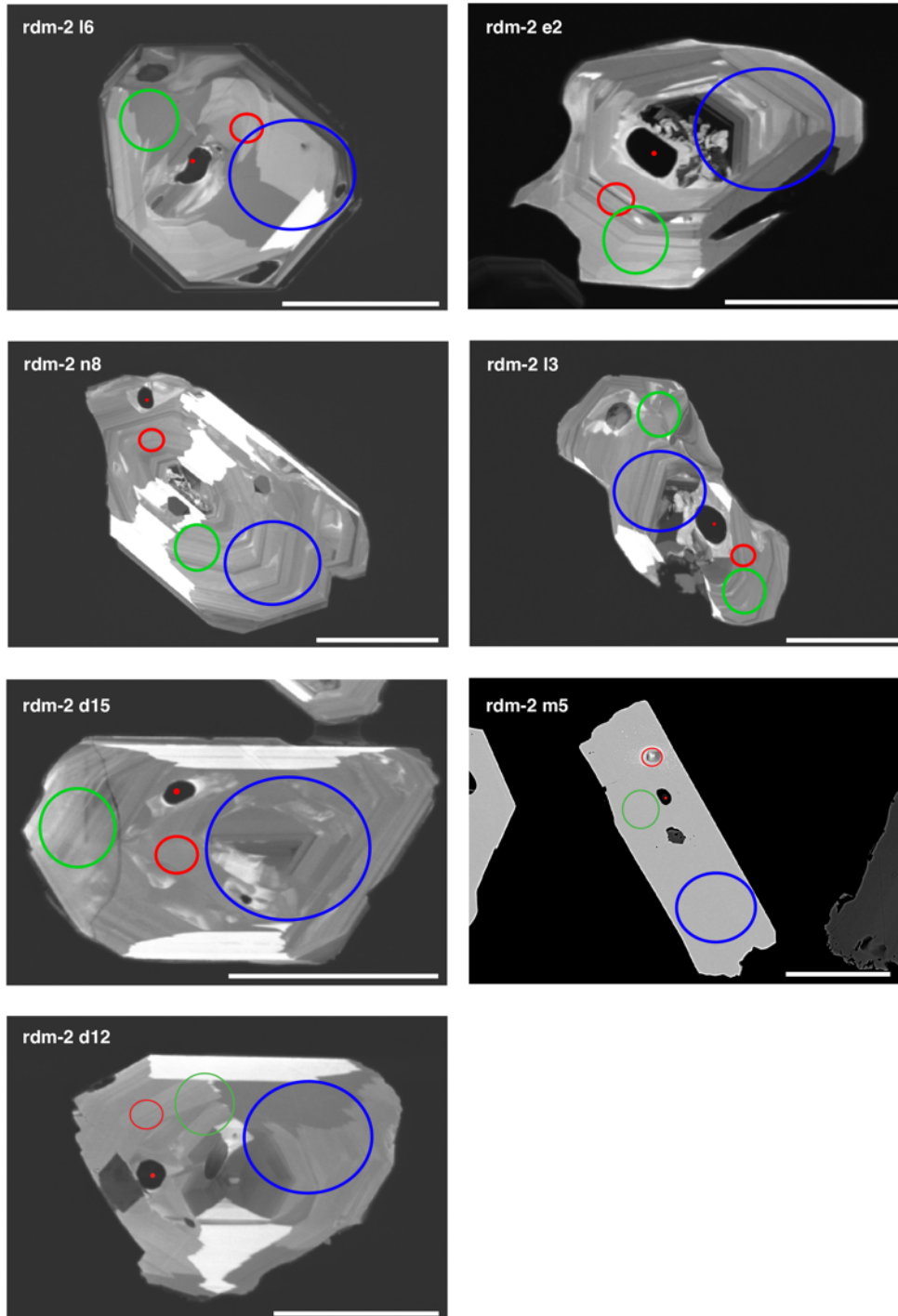
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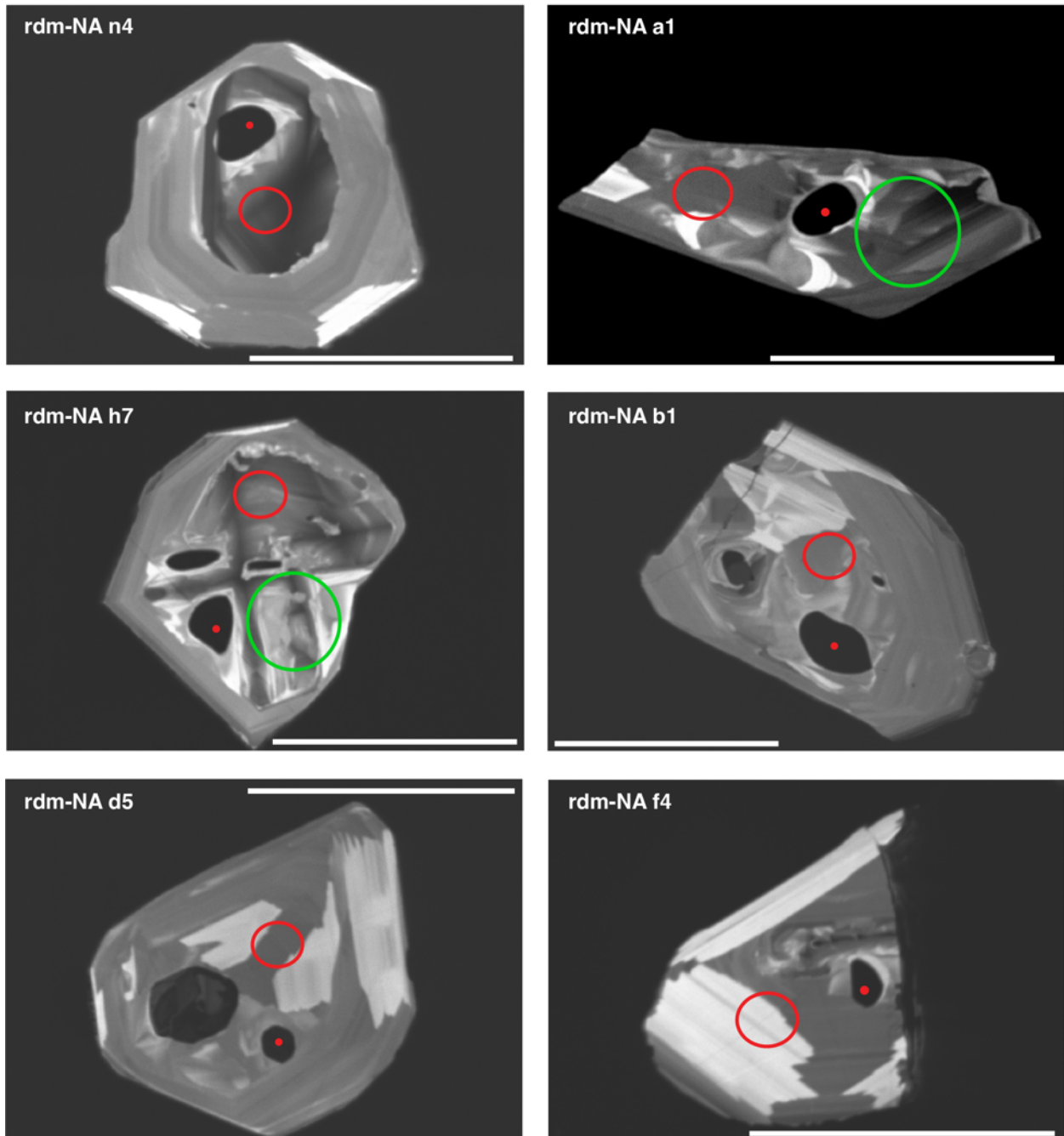
680 Figure S1-1. CL images of younger rdm zircons (scale bars = 50 μm). Red dots indicate locations
681 of SIMS pits from the analyses of $\delta^{18}\text{O}/\text{H}_2\text{O}$ of the MIZs, while the red and green circles indicate
682 those from the $\delta^{18}\text{O}$ and trace element analyses of the zircons, respectively. Blue circles
683 indicate locations of SHRIMP pits from the ^{230}Th - ^{238}U age dating of the zircons.

● $\delta^{18}\text{O}/\text{H}_2\text{O}$ (MIZ)
 ○ $\delta^{18}\text{O}$ (Zrn)
 ○ Trace elements (Zrn)
 ○ ^{230}Th - ^{238}U age (Zrn)

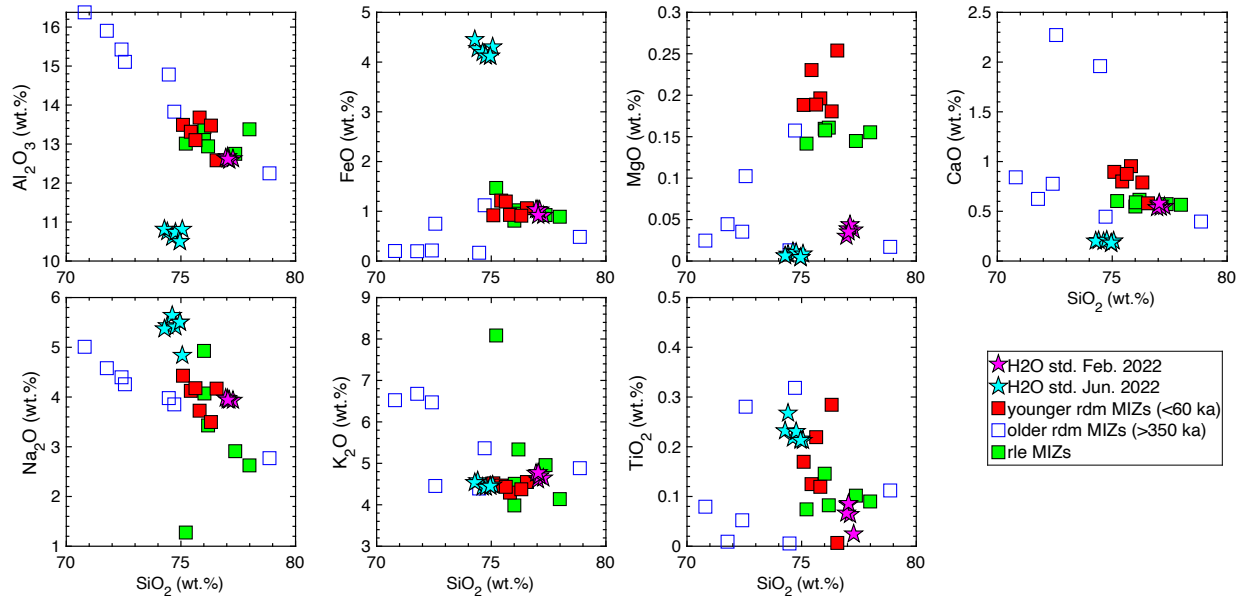


684
 685 Figure S1-2. CL images of older rdm zircons (scale bars = 50 μm). Red dots indicate locations of
 686 SIMS pits from the analyses of $\delta^{18}\text{O}/\text{H}_2\text{O}$ of the MIZs, while the red and green circles indicate
 687 those from the $\delta^{18}\text{O}$ and trace element analyses of the zircons, respectively. Blue circles indicate
 688 locations of SHRIMP pits from the ^{230}Th - ^{238}U age dating of the zircons.

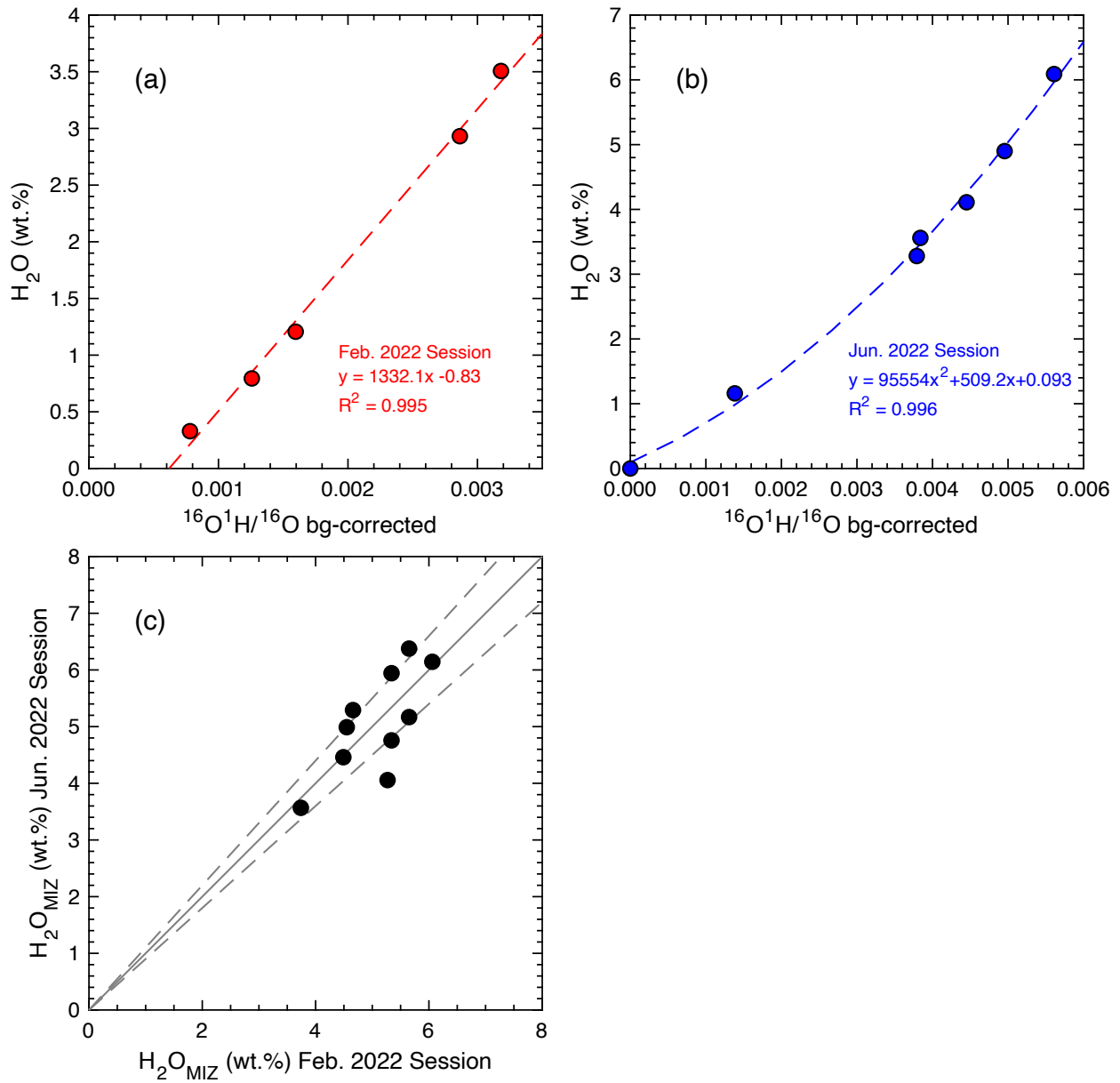
● $\delta^{18}\text{O}/\text{H}_2\text{O}$ (MIZ) ○ $\delta^{18}\text{O}$ (Zrn) ○ Trace elements (Zrn)



689
 690 Figure S1-3. CL images of rdm zircons with no ^{230}Th - ^{238}U ages (no age rdm zircons) (scale bars =
 691 50 μm). Red dots indicate locations of SIMS pits from the analyses of $\delta^{18}\text{O}/\text{H}_2\text{O}$ of the MIZ,
 692 while the red and green circles indicate those from the $\delta^{18}\text{O}$ and trace element analyses of the
 693 zircons, respectively.



694
 695 Figure S2. Harker diagrams showing the major element composition of the rdm and rle MIZs
 696 and the rhyolitic glasses standards with known H₂O concentrations (Newman et al. 1986; Singer
 697 et al. 2014b; Klug et al. 2020) that was used for SIMS H₂O calibration.

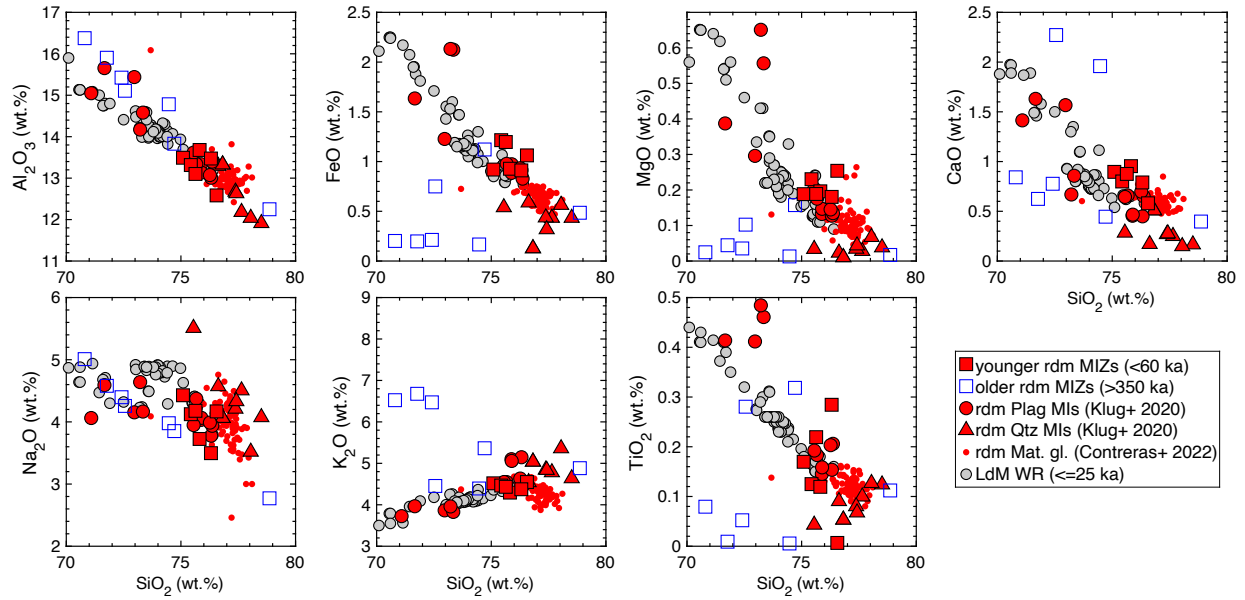


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699 Figure S3. SIMS H₂O calibration curves from (a) February 2022 and (b) June 2022, and (c)

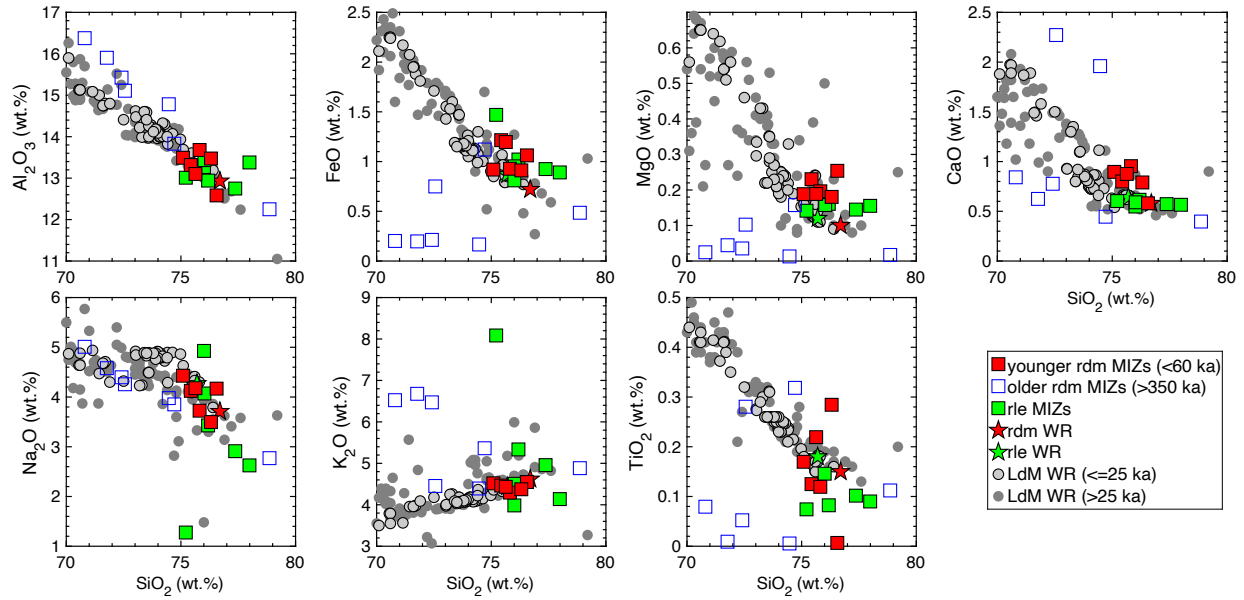
700 comparison of H₂O contents measured in identical MIZs measured during the two sessions. In

701 (c), the solid line is a 1:1 line and the dashed lines show $\pm 10\%$ deviation from the 1:1 line.



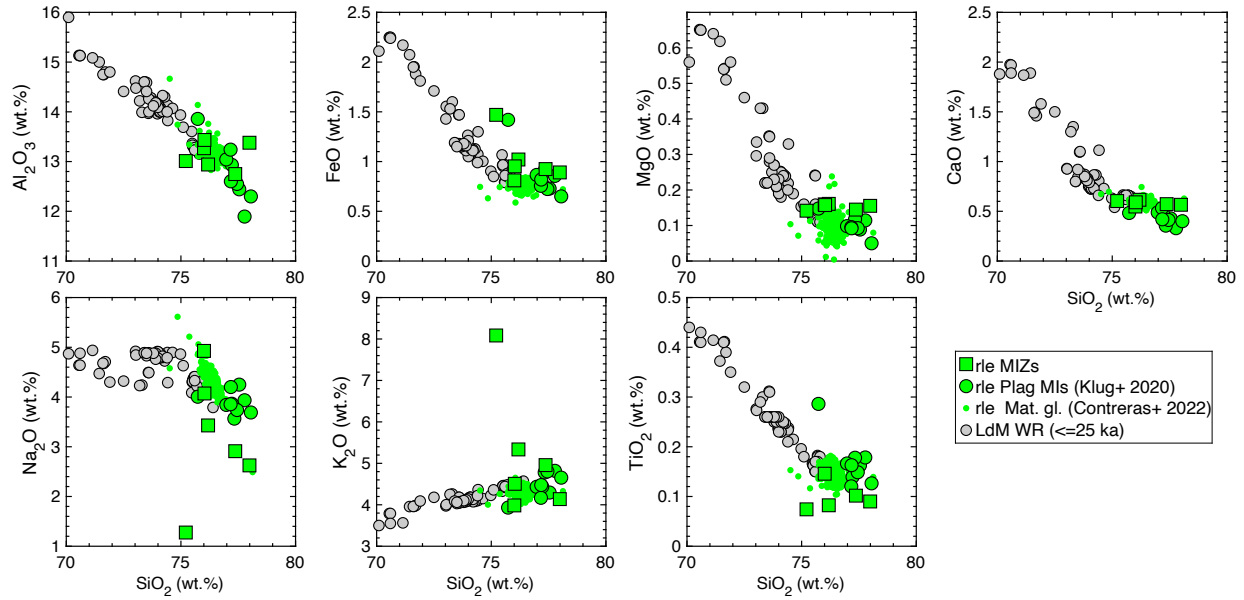
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Figure S4. Harker diagrams showing the major element composition of the rdm MIZs and correlated matrix glass data (Contreras et al. 2022), and melt inclusions in plagioclase and quartz data (Klug et al. 2020). Whole rock data of younger units (≤ 25 ka) from Andersen et al. (2017) and Hildreth et al. (2010) are also shown. MIZ and melt inclusions in plagioclase and quartz compositions are normalized to 100% on anhydrous basis to allow direct comparison with the whole rock data (and matrix glass that is dehydrated through the eruption process).



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Figure S5. Harker diagrams showing the major element composition of the rdm and rle MIZs and correlated whole rock compositions. Whole rock data of younger units (≤ 25 ka) are from Andersen et al. (2017), Hildreth et al. (2010), and Contreras et al. (2022) and those of older units (> 25 ka) are from Hildreth et al. (2010). MIZ compositions are normalized to 100% on anhydrous basis to allow direct comparison with the whole rock data.



716
 717 Figure S6. Harker diagrams showing the major element composition of the rle MIZs and
 718 correlated matrix glass data (Contreras et al. 2022), and melt inclusions in plagioclase data (Klug
 719 et al. 2020). Whole rock data of younger units (<=25 ka) from Andersen et al. (2017) and
 720 Hildreth et al. (2010) are also shown. MIZ and melt inclusions in plagioclase compositions are
 721 normalized to 100% on anhydrous basis to allow direct comparison with the whole rock data
 722 (and matrix glass that is dehydrated through the eruption process).

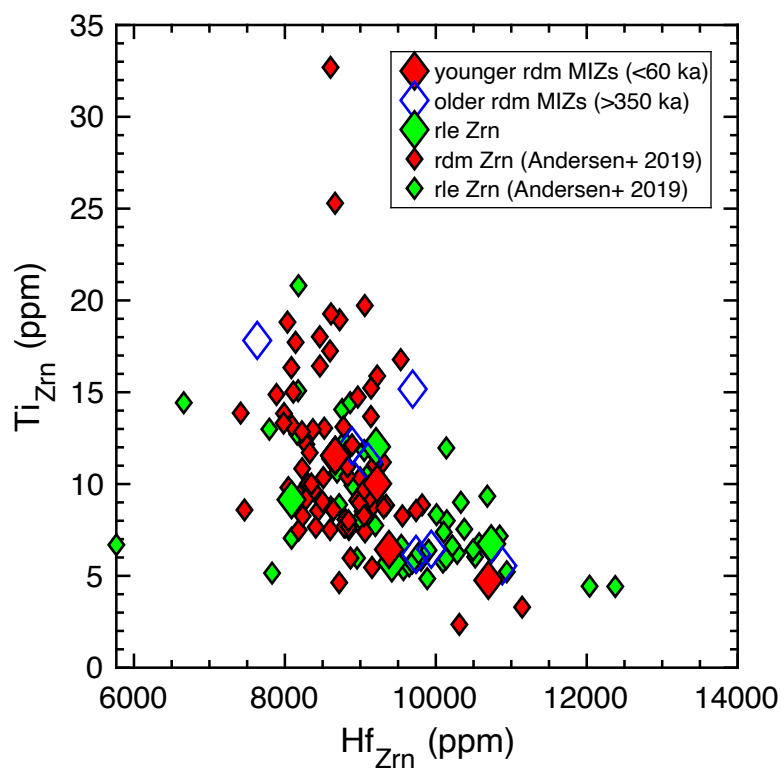
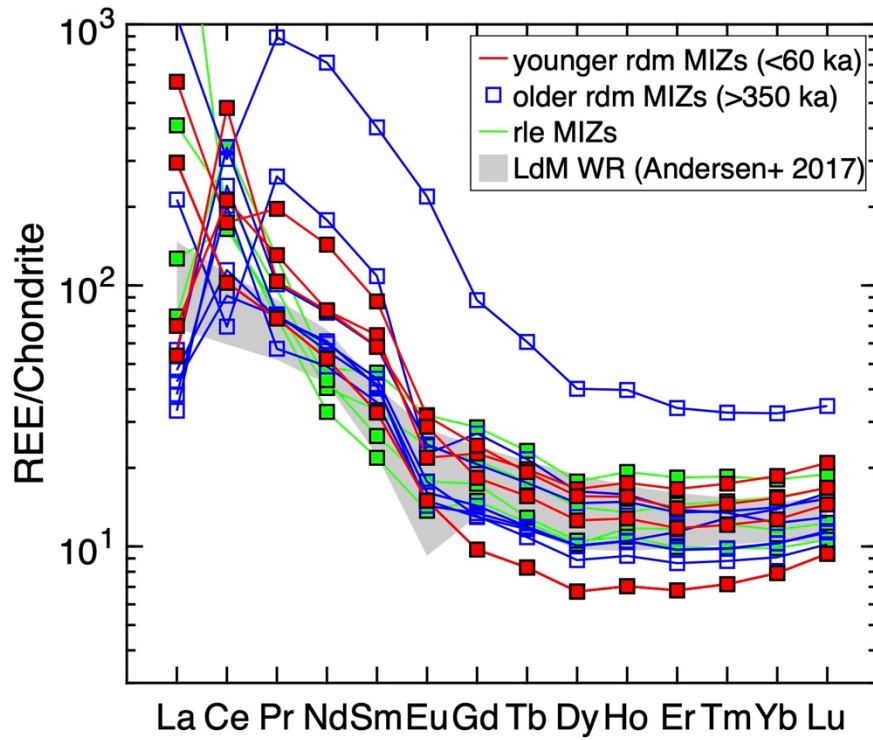


Figure S7. Ti vs. Hf of the rdm and rle zircons.



725
 726 Figure S8. Chondrite normalized REE pattern of melts in equilibrium with younger rdm, older rdm,
 727 and rle zircons. Calculated using the zircon-melt REE partition coefficients from Sano et al. (2002).
 728 Shown for comparison are the LdM whole rock data (Andersen et al. 2017). Chondrite REE values
 729 are from McDonough and Sun (1995).

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