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Author(s): <u>Szymanowski, Dawid</u> (b; Ellis, Ben S.; <u>Wotzlaw, Jörn-Frederik</u> (b; Bachmann, Olivier

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Maturation and rejuvenation of a silicic magma reservoir: high-resolution chronology of the Kneeling Nun Tuff

4 Dawid Szymanowski, Ben S. Ellis, Jörn-Frederik Wotzlaw, Olivier Bachmann

Institute of Geochemistry and Petrology, Department of Earth Sciences, ETH Zürich, Clausiusstrasse 25, 8092 Zürich, Switzerland; dawid.szymanowski@erdw.ethz.ch

Abstract

Knowledge of the conditions of magma storage prior to volcanic eruptions is key 8 9 to their forecasting, yet little is known about how melt compositions, crystallinity and intensive parameters within individual magma reservoirs evolve 10 over time. To address this, we studied the Kneeling Nun Tuff, a voluminous 11 12 (>900 km³) deposit of an Eocene caldera-forming eruption from the Mogollon-Datil volcanic field in New Mexico, USA. Whole-rock, feldspar and amphibole 13 compositions were combined with zircon trace-element geochemistry and 14 precise isotope dilution-thermal ionisation mass spectrometry (ID-TIMS) U-Pb 15 zircon crystallisation ages to arrive at a detailed, time-resolved record of 16 17 chemical and physical changes within the voluminous, upper-crustal (~2.2 kbar) magma reservoir. Chemical compositions and zircon ages of the Kneeling Nun 18 Tuff and co-magmatic clasts hosted within it reveal prolonged (>1.5 million 19 years) growth and maturation of the magma reservoir that was heterogeneous in 20 terms of temperature, melt composition and crystallinity. This protracted storage 21 at a dominant crystallinity in excess of 50% culminated in a period of ca. 50 ky 22 23 of increase in recharge heat supply and related homogenisation, decrease in crystallinity to 40-50%, and potential increase in average melt temperature, 24 leading up to eruption at 35.299 ± 0.039 Ma. Sampling of co-magmatic lithic 25 clasts derived from early-cooled domains of the reservoir show that the long, 26 million year-scale maturation time is shared across all erupted domains of the 27 magmatic system, irrespective of their final cooling history. This study provides 28 key observations from a natural system against which thermal and mechanical 29 models of upper-crustal magma reservoir construction can be validated. 30

31 **1. Introduction**

Explosive volcanic eruptions can have tremendous effects on both the Earth system and 32 society, ranging from local-scale devastation to global perturbations of the climate system 33 caused by release of volcanic gases (Self, 2006). Understanding how magma bodies 34 35 feeding such eruptions work, as well as achieving the long-term goal of forecasting eruptions, crucially depends on the knowledge of the mode of magma storage (e.g. 36 crystallinity, temperature, pressure, volatile content, all affecting its physical properties) 37 and the timescale of the system's maturation prior to eruption. The physical state of a 38 magma reservoir is key in the context of detecting such bodies by geophysical methods in 39 the present day as well as reading their readiness to erupt (e.g. Flinders et al., 2018; Kiser 40 et al., 2018). In turn, the temporal aspect of magma residence feeds into a better 41 understanding of magmatic fluxes, eruption frequencies and magnitudes (Costa, 2008). It 42 is particularly important to know how magma parameters vary over time, e.g. whether the 43 baseline (dormancy) magma storage conditions need to be drastically altered in a lead-up 44 45 to an eruption, as proposed for silicic, high-crystallinity systems (Bachmann and Bergantz, 2003). Therefore, our understanding of upper-crustal magmatic processes 46 would benefit from a detailed, absolute chronology of physical and chemical fluctuations 47 in a fossil magma reservoir. Such a record has the potential to bring new insights about 48 the magnitude, character and duration of key events in a magmatic system's life. 49

Ideally, such a chronology could be extracted from the most abundant, major mineral phases such as feldspar, pyroxene or quartz. However, the often-detailed stratigraphy of events preserved as compositional zoning in these phases carries little information that can be placed in absolute time. Given the relatively fast diffusion of most major and trace elements in these phases at magmatic temperatures (often utilised to constrain diffusion timescales; Costa et al., 2008), the compositions of the measured crystals will represent

partial equilibration i.e. the conditions of crystallisation modified by any subsequent 56 diffusion. Using independent estimates of the temperature of storage of a crystal, 57 diffusion modelling can then be used to constrain the maximum amount of time spent in 58 magma at given conditions (Cooper and Kent, 2014). This approach is capable of 59 delivering important insights about the thermal history of individual crystals since a given 60 (e.g. rim) crystallisation event, but currently cannot constrain the age of crystallisation 61 itself. The only absolute, high-temperature chronometer for major phases applicable to 62 63 this problem relies on U-series disequilibria and requires analysing large separates of minerals from young rocks, which results in complex averaging effects (Cooper, 2015). 64 As a consequence, building a reliable chronology of pre-eruptive events using the most 65 abundant and sensitive, major mineral phases remains challenging. 66

An alternative is to focus on zircon, a common accessory phase in silicic igneous rocks. 67 Due to extremely slow diffusion of most trace elements (Cherniak and Watson, 2003), 68 zircon crystals faithfully record melt composition and changes in intensive parameters 69 while allowing them to be placed in a temporal framework using the U-Pb chronometer. 70 Such approaches have been used for young magmatic rocks mostly in the ²³⁰Th-²³⁸U 71 disequilibrium range (Vazquez and Reid, 2004; Stelten et al., 2013; Barboni et al., 2016; 72 Tierney et al., 2016; Kaiser et al., 2017) but it has been shown that in some cases the 73 interpretations may be non-unique primarily due to poor precision of individual zircon 74 75 ages when compared to the expected duration of the events (Kent and Cooper, 2017). While *in situ*²³⁰Th-²³⁸U dating is the method of choice for magmatic systems younger 76 than ca. 400,000 years, the majority of the most voluminous eruptions in the geological 77 record and all known plutons are significantly older, requiring alternative analytical 78 approaches. For such cases, zircon geochronology by isotope dilution-thermal ionisation 79 80 mass spectrometry (ID-TIMS) has been shown to provide sufficient precision (typical single-crystal date uncertainties of <1 ‰) to resolve the timescales of magmatic 81

processes on the scale of a single magma body (e.g. Coleman et al., 2004; Schaltegger et 82 al., 2009). In particular, the combination of this technique with either bulk-grain or in situ 83 zircon chemical and isotopic information can yield time-composition systematics useful 84 in constraining large-scale changes of magmatic conditions (Schoene et al., 2012; 85 Wotzlaw et al., 2013; Rivera et al., 2014; Samperton et al., 2015).

86

Here we present a case study employing high-precision zircon U–Pb dating by ID-TIMS 87 to construct a detailed pre-eruptive chronology of events in a large magmatic system. We 88 studied the Kneeling Nun Tuff, a voluminous (> 900 km³) deposit of an Eocene super-89 eruption fed by a long-lived magmatic reservoir (Szymanowski et al., 2017) with both 90 traditional tools of petrology and detailed zircon petrochronology, allowing new insights 91 into the maturation and rejuvenation of magmas feeding such large-volume caldera-92 93 forming eruptions.

2. Kneeling Nun Tuff 94

95 The Kneeling Nun Tuff (KNT) is a voluminous ignimbrite emplaced within the Mogollon-Datil volcanic field (MDVF) in western New Mexico, USA (Fig. 1; McIntosh 96 et al., 1990; McIntosh et al., 1992; Chapin et al., 2004). The MDVF is part of a 97 discontinuous belt of mid-Tertiary silicic volcanic fields extending from the southern 98 Rocky Mountains in Colorado in the north (Lipman, 2007) to Sierra Madre Occidental in 99 central Mexico in the south (McDowell and McIntosh, 2012; Fig. 1a). The Mid-Tertiary 100 volcanic activity in this area was mostly characterised by an arc-like geochemical 101 signature (high-K calc-alkaline series) related to the subduction of the Farallon plate 102 beneath North America, however the large distance from the plate margin in present 103 Colorado and New Mexico would require this subduction to be of low angle (Lipman et 104 al., 1972; Coney and Reynolds, 1977). Alternatively, interpretations involving magma 105

106	generation from the sub-continental lithospheric mantle previously modified by
107	subduction have been proposed (Davis and Hawkesworth, 1993; Farmer et al., 2007).
108	MDVF activity followed a pattern similar to other Tertiary volcanic fields of SW North
109	America, where early intermediate volcanism was followed by voluminous caldera-
110	forming eruptions of silicic magma (cf. Lipman, 2007). In the MDVF, initial andesitic
111	volcanism dominated between 40-36 Ma before episodic bimodal basaltic andesite-
112	silicic activity became predominant between 36-24 Ma (Elston, 1984; McIntosh et al.,
113	1990; McIntosh et al., 1992). The Kneeling Nun Tuff (Elston, 1957) was erupted from
114	the Emory caldera (Elston et al., 1975) in the southern part of the Black Range at the SE
115	edge of MDVF (Fig. 1b) at 35.36 ± 0.05 Ma (recalculated from McIntosh et al., 1990)
116	and is considered the largest eruption of the first pulse of MDVF silicic volcanism
117	(McIntosh et al., 1992).

The Kneeling Nun Tuff occurs both in thick intracaldera facies (500-1000 m; Kuellmer, 118 1954; Elston et al., 1975) and outflow facies (up to 150 m thick) extending at least 30 km 119 beyond the caldera margins (Fig. 1b). This extent led to a minimum eruptive volume 120 estimate of 900 km³ (Elston et al., 1975) placing the KNT among the largest silicic 121 eruptions in the geological record (Mason et al., 2004). The KNT outflow typically forms 122 conspicuous, columnar-jointed red cliffs of welded ignimbrite (Fig. 2a), which are often 123 subdivided by local breaks into multiple 'cooling units' reflecting the complex nature of 124 pyroclastic density currents and effects of variable topography (e.g. Giles, 1965). The 125 KNT typically overlies a thick sequence of broadly andesitic lavas and tuffs of the Rubio 126 Peak formation, but locally a sequence of rhyolitic ignimbrites and air fall tuffs mapped 127 as the Sugarlump Formation occurs beneath the KNT (Elston, 1957). Dated at $35.64 \pm$ 128 0.12 Ma (recalculated from McIntosh et al., 1990), some of the Sugarlump tuffs may 129 represent precursor eruptions from the same magmatic system that fed the KNT. 130

The Kneeling Nun Tuff is a crystal-rich (trachy)dacite to rhyolite carrying a mineral 131 assemblage of quartz + sanidine + plagioclase + biotite + hornblende + rare 132 clinopyroxene + magnetite + ilmenite + titanite + apatite + zircon. The reported crystal 133 content is between 25 and 60% (Giles, 1965). The KNT outflow sheets are locally zoned, 134 with an upward increase in crystallinity, phenocryst size and the proportion of plagioclase 135 and ferromagnesian phases accompanied by a decrease in the amount of quartz and alkali 136 feldspar (Giles, 1968). Both outflow and intracaldera KNT facies contain abundant 137 138 crystal-rich pumice, rare crystal-poor pumice and xenoliths of underlying Rubio Peak andesites, Palaeozoic basement rocks, and granites, porphyries and aplites of variable 139 texture which may be partly contemporaneous and genetically related to KNT magma 140 (Elston, 1989). Abundant cm-sized xenoliths are present throughout the ignimbrite but in 141 some areas within the caldera they become larger (up to tens of metres) and form zones of 142 143 'megabreccia' that were previously interpreted as vent or collapse breccias (Kuellmer, 1954; Elston, 1989). 144

145 **3. Samples**

A total of 26 samples of different facies of the Kneeling Nun Tuff have been studied,
comprising two main groups:

148 1) Samples of bulk KNT ignimbrite from the SW (Lucky Bill Canyon) and E (Tierra

Blanca) outflow sheets as well as the caldera fill (Fig. 1), ranging from early- to late-

erupted material. Detailed studies of the two outflow sections (Table 1; Supplementary

151 Fig. 2) are complemented by samples used only for bulk chemical analyses

152 (Supplementary Tables 1, 2).

153 2) A suite of magmatic clasts of presumed cogenetic character found within both

intracaldera and outflow facies of the ignimbrite (Table 1, Fig. 1). The samples were

assigned to one of three groups: i) pumices, which have clear indications of ductile
behaviour upon deposition (ubiquitous flattening, Fig. 2b), ii) porphyries, containing
large phenocrysts in a formerly glassy matrix, but without clear evidence of syndepositional deformation (Fig. 2d, e), and iii) plutonic lithics—angular fragments of
holocrystalline, porphyritic to equigranular granites (Fig. 2c, f).

160 **4. Analytical Methods**

The samples were characterised by a combination of bulk chemical analyses, major
 element chemistry of main rock-forming mineral phases (feldspars, amphibole) and *in*

situ trace element analyses of accessory zircon, followed by high-precision U–Pb isotope

analyses of the same, partly polished down, zircon crystals.

165 Whole-rock compositions were determined following standard procedures by X-ray

166 fluorescence (XRF) of fused glass beads with complementary laser ablation–inductively

167 coupled plasma mass spectrometry (LA-ICPMS) analyses of trace elements. Feldspar and

amphibole major elements were analysed in thin sections by electron probe microanalysis

169 (EPMA). A subset of feldspar crystals was also analysed for trace elements by LA-

170 ICPMS.

171 In order to obtain a time-resolved record of the KNT magma storage regime, a particular

focus was placed upon studying the textures, compositions and crystallisation ages of

173 zircon crystals separated from magmatic clasts found within the ignimbrite. The

analytical approach taken here is identical to that presented by Szymanowski et al.

175 (2017), which allows a direct comparison of zircons separated from a bulk ignimbrite

sample with those hosted by the various types of clasts. First, the zircons were mounted

in epoxy, polished and imaged using cathodoluminescence (CL), which was followed by

in situ analyses by LA-ICPMS for trace elements and U–Pb isotopes to screen out

179	inherited cores. Particular care was taken to ensure the accuracy of Ti analyses, which
180	was made possible by the introduction of the Ti-rich zircon reference material GZ7
181	(Szymanowski et al., 2018). Based on zircon compositions determined in situ and their
182	CL textures, some crystals were selected for extraction from the epoxy mounts for
183	dissolution and high-precision U-Pb analyses by chemical abrasion (CA)-isotope
184	dilution-thermal ionisation mass spectrometry (ID-TIMS).
185	A complete description of all analytical procedures as well as tables with sample

186 coordinates and all analytical data are provided as Supplementary Material.

187 **5. Results**

188 5.1. Whole-rock compositions and crystallinity

Bulk samples of KNT ignimbrite range in composition from (trachy-)dacite to rhyolite 189 190 (67-77 wt% SiO₂, Supplementary Fig. 1 and Table 1) with crystallinities of 32-58% (11% in the basal fallout). Of the two outflow sections studied in detail (Fig. 1), one 191 (Lucky Bill Canyon; samples 1519–1523) displays clear, systematic variations from 192 193 early-erupted, evolved (>70 wt% SiO₂), less crystalline material to crystal-rich (46–55%), (trachy-)dacitic (67-69 wt% SiO₂), late-erupted material towards the top of the section 194 (Supplementary Fig. 2). The other section (Tierra Blanca; samples 1428–1435) does not 195 show any substantial variability in compositions, but the earliest-erupted material is 196 similarly crystal-poor. Key major and trace elements are characteristically correlated with 197 SiO₂ (Supplementary Fig. 1), and their trends are indicative of fractionation of feldspars, 198 hornblende, Fe-Ti oxides, titanite, zircon and apatite, consistent with the observed 199 mineral assemblage. The variability between early-erupted and late-erupted compositions 200 201 can therefore be fully explained in terms of variable melt extraction and crystal accumulation within the upper-crustal magma reservoir. All sampled KNT-hosted clasts 202

define the same compositional array (Supplementary Fig. 1), with the bulk compositions
 corresponding to their mineral assemblage and crystallinity.

205 5.2. Feldspars

206	Feldspar occurs in the KNT as fragments of mostly euhedral plagioclase and sanidine that
207	show little major element variability within individual crystals, samples, between parts of
208	the deposit, or within the juvenile/lithic clasts (Table 1; Supplementary Figs 3, 4).
209	Plagioclase ranges mostly between An_{20} and An_{28} with rare cores of up to An_{51} ,
210	presumably inherited from deeper differentiation steps. An contents lower than ~ 20 are
211	present exclusively in early-erupted material (samples 1519–1521, 1428), the crystal-poor
212	pumice (1434) and the plutonic lithics (1421, 1510). Sanidine displays similarly little
213	variability in major elements (Table 1; Supplementary Figs 3, 4); typical compositions
214	are Or_{61-66} , with notable exceptions of elevated K in the porphyritic samples (1416A,
215	1509A, 1511; Or_{64-69}) and the basal fallout (1519, Or_{69-71}). Corresponding two-feldspar
216	pairs reveal equilibrium temperatures (Putirka, 2008) of ~730-820 °C for most late-
217	erupted material, crystal-rich pumice and porphyritic clasts, while the crystal-poor
218	pumice, all early-erupted material and plutonic lithologies return lower temperatures
219	ranging from ~760 °C down to 640 °C (in the basal fallout; Table 1, Supplementary Fig.
220	2).

An additional feature of KNT sanidine is the common occurrence of one or more growth rims, present either as simple growth zones or surrounding a resorbed core, that are enriched in Ba (Fig. 3). The rims occur in most late-erupted parts of the ignimbrite as well as the porphyritic clasts, but are seemingly lacking in early-erupted and evolvedcomposition samples (Table 1). Their BaO contents are up to 2 wt% (Supplementary Table 3); representative trace element data (Fig. 3) show that increased Ba is accompanied by enrichments in elements compatible in the bulk mineral assemblage such as Sr, Ti, P and REE and depletions in the incompatible Rb. Additionally, Pb-isotopic
compositions of these rims tend to be somewhat less radiogenic than the respective cores
(Szymanowski et al., 2017).

231 *5.3. Amphibole*

Except for rare (n=5) cores of tschermakitic composition, all of the analysed amphibole 232 crystals across bulk ignimbrite, pumice and porphyritic clast samples (n=115) are Mg-233 234 hornblendes with a very restricted compositional range and no clear zoning within individual crystals (Supplementary Table 4). The dominant, homogeneous population of 235 hornblende satisfies criteria for equilibrium with the corresponding plagioclase at 236 temperatures between 700-810 °C (Holland and Blundy, 1994), consistent with two-237 feldspar thermometry (Table 1) as well as the results of zircon- and titanite-based 238 thermometry (Szymanowski et al., 2017). Given the low-variance, near-solidus mineral 239 assemblage of KNT, we applied the revised Al-in-hornblende geobarometer of Mutch et 240 al. (2016), which yields a uniform pressure estimate of 2.22 ± 0.10 kbar (1 σ) for the 241 equilibrium hornblendes. The rare higher Al tschermakitic cores crystallised at pressures 242 of 3-4 kbar and are interpreted as representing deeper stages of differentiation of magmas 243 feeding the shallow KNT reservoir. 244

245 5.4. Zircon

246 5.4.1. Textures

247 Zircon crystals from the bulk KNT ignimbrite and the clasts hosted within it are typically

euhedral and prismatic irrespective of the sample lithology (Fig. 4). Nearly all grains

249 display complex oscillatory (and rare sector) zoning testifying to their complex

crystallisation histories. A subset of zircons, found in samples 1402, 1525-2 and 1509A,

is characterised by large size (up to $>500 \mu m$ length), simple zonation patterns and

conspicuously high CL intensities (Fig. 4) correlating to low rare earth element (REE)
contents (section 5.4.3).

254 5.4.2. High-precision U–Pb geochronology

ID-TIMS U-Pb dating was performed on single zircons extracted from three kinds of 255 magmatic clasts; pumices (2 samples), porphyries (3 samples), and plutonic lithics (2 256 samples; Fig. 5). The targeted crystals were pre-screened for inherited cores and 257 inclusions based on CL imaging and *in situ* chemical analyses and except for one dated 258 zircon (1416A z21) did not show any indication of inheritance. With the exception of one 259 of the plutonic clasts (1510-1) which is distinctly older than the remaining samples, the 260 ranges of individual zircon dates from each clast overlap to a large degree both between 261 samples and with the bulk outflow ignimbrite zircons analysed previously by 262 Szymanowski et al. (2017). This supports field relationships between the clasts and the 263 hosting Kneeling Nun Tuff and confirms that all overlapping samples, and likely also the 264 granitic clast 1510-1, are sourced from the same upper-crustal magmatic system. The re-265 sampling of this system additionally confirms its longevity, with the zircon from clast 266 samples spanning ranges of U–Pb dates from 341 ± 20 ky to as much as 1.22 ± 0.14 My, 267 broadly comparable to 618 ± 56 ky obtained for the bulk ignimbrite. 268 269 The Kneeling Nun Tuff eruption age can now be defined as either the Th-corrected 206 Pb/ 238 U date of the single youngest zircon (35.305 ± 0.021/0.024/0.045 Ma) or a 270 Bayesian estimate (Keller et al., 2018) using a bootstrapped prior distribution based on 271 data from juvenile samples, yielding $35.299 \pm 0.039/0.040/0.056$ Ma (2σ uncertainty 272 given as internal only/with tracer calibration/with ²³⁸U decay constant). The two estimates 273 are indistinguishable and both are fully consistent with the existing 40 Ar/ 39 Ar sanidine 274 dates of the KNT (McIntosh et al., 1990) recalculated to the more recent standard and 275 decay constant calibration of Kuiper et al. (2008; Fig. 5). The ⁴⁰Ar/³⁹Ar age of the 276

uppermost Sugarlump tuffs (McIntosh et al., 1990) overlaps with most of the zircon
crystallisation interval, suggesting a genetic relationship between at least some of the
Sugarlump eruptions and the KNT.

280 Individual dates of zircons from both pumice samples (the evolved, high-Si 1434A, and the low-Si 1525-2) range from ones close to, or overlapping, eruption age at $35.299 \pm$ 281 0.039 Ma and up to a maximum of 36.077 ± 0.023 Ma (Fig. 5). While the number of 282 analysed zircons is smaller (n=8) and consequently the sampled populations are less 283 representative than the large bulk ignimbrite dataset, the pumices preserve an 284 285 indistinguishable age distribution, suggesting that they sample a comparable age domain. In contrast to the pumices, the textures of the porphyries imply rapid cooling of these 286 magma volumes some time before eruption. This appears true for all three porphyry 287 samples as they record the same time of peak zircon crystallisation and apparent pre-288 eruptive gaps in zircon distributions of 67 ± 49 , 134 ± 42 and 291 ± 45 ky. However, one 289 exception is that sample 1509A contains one young zircon with a date overlapping the 290 eruption age. The plutonic samples, consistently with textures requiring slow cooling pre-291 dating the eruption, only contain zircons with crystallisation ages significantly older than 292 293 the eruption age. The granitic clast 1421, similarly to porphyry samples, records zircon crystallisation coeval with that found in pumices and in bulk ignimbrite, but with a pre-294 eruptive gap of 168 ± 41 ky. Clast 1510-1 represents an early period of intrusion with 295 296 zircon crystallisation ages from 36.896 ± 0.082 to 36.653 ± 0.025 Ma. These granitic clasts show that during most of the time of magma reservoir assembly, portions of the 297 reservoir were fully solid, forming 'cool' wall-rock around the active, eruptible domains. 298

299 5.4.3. Trace elements

Trace elements in KNT zircons (Fig. 6, Supplementary Figs 5, 6) show large variability consistent with the complex CL textures and the complexity expected from sampling

302	domains of the magmatic system with different thermal histories. The zircon
303	compositions testify to the key control exerted by co-crystallising titanite and, to a lesser
304	degree, hornblende over REE budgets, which can be shown with simple geochemical
305	models (Szymanowski et al., 2017) for both REE contents and heavy/middle REE ratios
306	(e.g. Yb/Dy). Strong correlations exist between titanite indicators (e.g. MREE or Th/U)
307	and the temperature-dependent Ti contents (Ferry and Watson, 2007). This is particularly
308	the case for low-Ti zircons, suggesting relatively low-T titanite saturation. Zr-in-titanite
309	thermometry (Szymanowski et al., 2017), recalculated to the amphibole pressure of 2.2
310	kbar, places titanite saturation for KNT at around 734 °C.
311	Combining trace elements with bulk-grain crystallisation ages (Fig. 6) reveals a complex
312	history of zircon crystallisation within the KNT magma reservoir. While individual
313	samples do not provide sufficient data points to evaluate any temporal trends, all data
314	taken together reveal important reservoir-scale systematics. For most of the reservoir's
315	lifetime, the zircons are characterised by significant compositional scatter with dominant
316	low-T, evolved compositions (e.g. Eu/Eu* of 0.2–0.5, Ti: 3-10 ppm, Dy <200 ppm)
317	punctuated by analyses indicating both higher temperature (high Ti), less-evolved melts
318	(e.g. high Eu/Eu*, Dy, low Yb/Dy) and lower temperature, more-evolved melt
319	compositions (low Ti, Eu/Eu*, Dy, high Yb/Dy). The sense of measured zonation within
320	individual crystals is highly variable, with inner zones ('cores' in Supplementary Figs 5,
321	6) generally showing more scatter than rim compositions. However, the CL-bright,
322	texturally simple crystals (Fig. 4) with bulk U–Pb ages between \sim 35.35 Ma and eruption
323	age at 35.299 Ma exhibit a striking compositional focussing trend towards increased
324	Eu/Eu* (0.3–0.7), Ti (6–19 ppm) and variably decreased REE (e.g. Dy <150 ppm, Yb
325	<500 ppm), Yb/Dy (<6) (Fig. 6). The observation of this compositional trend across three
326	separate samples suggests a critical change in magmatic storage conditions that affected
327	large portions of the magma reservoir in the last \sim 50 ky before eruption.

328 6. Discussion

329 6.1. Magmatic architecture and storage conditions determined from major

330 *mineral phases*

Compositions of major mineral phases in the Kneeling Nun Tuff constrain the dominant 331 magma storage conditions to a pressure of ~ 2.2 kbar (ca. 7–9 km depth) and temperatures 332 between ~670 °C and 820 °C (Table 1), consistent with its near-solidus mineral 333 assemblage. Pre-eruptive crystallinity of the dominant volume of erupted magma (as 334 documented in the late-erupted samples) appears to have been on the order of 40-50%, 335 but locally or episodically reached values in excess of 60% (Table 1). Such high 336 crystallinity may imply rheological lock-up in the form of a rigid crystal mush, which 337 338 facilitates the long-term survival of the magma body but requires a process eventually reducing the crystal content for most of the reservoir volume to erupt (Marsh, 1981; 339 Bachmann et al., 2002; Bachmann and Bergantz, 2003). Locally melts would get 340 extracted from the mush zone, creating pools of more evolved, crystal-poor material, 341 represented by crystal-poor pumice (1434), the basal fallout (1519) and, as variable 342 mixtures with crystal-rich material, in early-erupted magma (Table 1). 343 Amphibole and feldspar compositions, as well as those of bulk rock (Supplementary Fig. 344 1), reveal large-scale compositional homogeneity of the KNT magma reservoir. Most of 345 the variability in whole-rock compositions is attributable to variable mineral proportions 346 and crystallinity, while all deviations in feldspar major element compositions and 347 temperatures (Table 1) could result from either 1) local melt extraction or 2) variable 348 349 cooling of different domains sampled by clasts. In particular, the lowest An contents of plagioclase are associated with extracted melts either in the evolved pumice (1434), in all 350 early-erupted material, or in the slowly-cooled plutonic clasts (Supplementary Fig. 4). 351

Similarly, all deviations to higher orthoclase contents of K-feldspars occur either in 352 extracted melts (1519) or in porphyry samples which presumably did not readjust their 353 compositions to predominant pre-eruptive conditions due to 'premature' solidification. 354 355 The occurrence of high-Ba rims in sanidine (Fig. 3) requires the episodic presence of melts enriched, with respect to background values of melt in equilibrium with most of 356 sanidine volume, in Ba and other bulk-compatible elements (Section 5.2). Such 357 compositions can generally be expected as a result of either 1) recharge of the system 358 with less evolved melts, or 2) melting of the resident mush in response to a heat and 359 360 volatile addition, with the melting phase assemblage dictating the elemental enrichments (Wolff et al., 2015; Forni et al., 2016). In the KNT, the enrichments would require the 361 melting of cumulate sanidine + plagioclase (Ba, Sr), titanite (Ti, REE) and apatite (P), 362 363 most likely accompanied by quartz and biotite as low-temperature phases. The wide range of published partition coefficients for trace elements in sanidine are permissive of 364 very large enrichments even at equilibrium, precluding a unique interpretation; 365 additionally, it is doubtful that such cumulate-derived crystallisation reflects at all an 366 equilibrium process (e.g. Arzilli et al., 2018). In reality the generation of any cumulate 367 melt is likely caused by an influx of hotter recharge magma, so the two processes should 368 be expected to act together. In the KNT, the presence of ubiquitous, often multi-stage 369 high-Ba rims in the crystal-rich, late-erupted material as well as in the porphyry samples 370 371 (which presumably cooled down before eruption) suggest that recharge and cumulate melting are common and repeated processes. This is in line with the long-lived nature of 372 the KNT system, which requires a persistent influx of heat delivered through recharge 373 magma to remain thermally buffered over timescales of several hundred thousand years 374 (Szymanowski et al., 2017). 375

While the major mineral phases provide a relatively simple view of magmatic storage in 376 the KNT reservoir, it is crucial to emphasise which 'time slice' of the prolonged, million-377 year history of the magmatic system they represent. For feldspar and amphibole (or any 378 other magmatic mineral), the compositions of erupted crystals should represent 379 conditions at time of crystallisation modified by any subsequent diffusion. In these two 380 minerals, the retention of most major and trace elements at magmatic conditions is 381 relatively limited, and depends primarily on their post-crystallisation storage history 382 383 (Cooper and Kent, 2014). If storage temperatures can be estimated independently, one can model the storage time of individual crystals since a given (e.g. high-Ba rim) 384 crystallisation event, but this result remains relative to the assumptions made. For that 385 reason, in the following sections we focus on zircon petrochronology which can be used 386 to obtain a more faithful, time-resolved record of magma reservoir evolution. 387

388 6.2. Time-resolved record of magmatic storage and rejuvenation

Zircon trace element compositions can be interpreted in terms of changes in both melt 389 composition and intensive parameters such as temperature (Melnik and Bindeman, 2018). 390 Given the comparable timescales of zircon growth and diffusive equilibration (Watson, 391 1996; Cherniak and Watson, 2003), except for sector zones, zircon compositions are 392 393 expected to faithfully record the chemical and physical environment at time of growth. Consequently, with an understanding of the main factors controlling zircon chemistry, 394 both the temporal and the compositional information in zircon may be exploited to 395 construct a chronology of major pre-eruptive events in a magmatic system (e.g. Wotzlaw 396 et al., 2013; Barboni et al., 2016). In many cases, particularly for young rocks, the 397 398 analytical age resolution may not be adequate to resolve events with sufficient certainty (Kent and Cooper, 2017). In the case presented here for the Kneeling Nun Tuff, the 399 precision afforded by applying ID-TIMS dating (2o uncertainties on individual dates 11-400

401	177 ka) theoretically provides a chance to describe such systematics with highly precise
402	constraints in the time dimension. The main challenge of our approach lies in matching in
403	situ measured compositions with bulk-crystal U-Pb ages (Fig. 6). We chose to assign
404	compositional data to the age constraint of the respective sectioned crystal fragment,
405	which may to some extent obscure reservoir-scale systematics (if they exist) and mask
406	small-scale secular compositional variations for all but the youngest crystals. Crucially,
407	zircon crystals of age close to eruption are least likely to contain a significantly older
408	inner zone biasing the bulk-crystal age, so all of their trace element compositions,
409	including those of cores, can be considered robust. Even given the limitations of this
410	approach, the large dataset of such (variably biased) zircon composition-age pairs allows
411	us to draw first-order conclusions about the character, magnitude, and duration of magma
412	reservoir-wide processes, with a particular focus on the youngest, pre-eruptive events.
413	Figure 6 illustrates that in the KNT magma, and presumably in other long-lived magmatic
414	systems that experience recurring recharge, multiple physical conditions/melt
415	compositions can be present at any given time. In other words, the degree of magmatic
416	evolution, e.g. along a liquid line of descent, does not equate to time (cf. simply cooling
417	magmatic systems, e.g. Samperton et al., 2015). Instead, trace elements in KNT zircon
418	show that environments of varying temperature, crystallinity, or mineral proportions (e.g.
419	samples of cumulate character vs. extracted melts) can coexist and can ultimately be
420	sampled by the same eruption (Fig. 6, Supplementary Fig. 5, 6). The key trace element
421	trajectories depicted in Fig. 6 all show large variability in zircon compositions for most of
422	the system's lifetime, ranging from those corresponding to low-crystallinity, relatively
423	unevolved melts to some indicating highly fractionated, crystalline environments (mostly
424	innermost cores, Supplementary Fig. 6). However, after ~35.35 Ma, or ~50 ky prior to
425	eruption, the system appears to undergo a significant change exhibited in more focussed,
426	or systematically offset, compositions. The negative Eu anomaly (Eu/Eu*), primarily

427	controlled by crystallisation/melting of feldspar, records a notable shallowing towards the
428	eruption (Fig. 6a). At the same time, Dy and Yb/Dy, both controlled by titanite
429	crystallisation (i.e. in a titanite-saturated system, its crystallinity), record a shift towards
430	titanite undersaturation (Fig. 6c, d). The increase in the temperature-dependent Ti towards
431	the eruption may reflect an increase in melt temperature, assuming activities of Ti and Si
432	in the melt remain constant (Ferry and Watson, 2007). Alternatively, influx of less
433	evolved melts and the associated (non-modal?) melting of minerals may alter both the Ti
434	and Si activity in a way that is difficult to predict or model, which could result in both
435	completely masking (higher a_{TiO2} or lower a_{SiO2}) and strengthening (lower a_{TiO2}) the
436	potential signal of temperature increase.
437	To understand better the nature of the melts represented by the measured zircon
438	compositions, we modelled melts in equilibrium with all KNT zircons using a
439	temperature-dependent parametrisation of zircon-melt element partitioning that uses Ti-
440	in-zircon as a temperature proxy (Claiborne et al., 2018). This approximation, while
441	potentially strongly biased by the accuracy of Ti quantification, proves useful in
442	simulating the first-order control of temperature on partitioning (Fig. 7). Assuming that
443	differences in Ti represent real temperature variations, we inverted zircon trace element
444	compositions (Fig. 7a) to their corresponding melts (Fig. 7b). This resulted in melt
445	compositions that are broadly consistent with the KNT bulk rock trend, and display a
446	remarkable transition between relatively hot, titanite-undersaturated melts (low Yb/Dy,
447	high Dy in Fig. 7b) and relatively cold, near-solidus, titanite-saturated melts (high Yb/Dy,
448	low Dy). In the KNT, where REEs are almost exclusively controlled by titanite
449	(Szymanowski et al., 2017), trends towards melts with high Yb/Dy can be explained only
450	by co-crystallising titanite, while the reverse (to low Yb/Dy, high Dy) can be
451	accomplished by both mixing with less evolved melts and melting of pre-existing titanite.
452	At the same time, changes in Eu/Eu* (Fig. 6a) result in an identical interpretation for

feldspar crystallisation and melting. As a consequence, zircon compositions alone are
unable to discriminate between an influx of recharge melts and the melting of cumulates
caused by the heat delivered by the same process (Wolff et al., 2015).

Plotting the resulting melt compositions against time (Fig. 8) creates a record of highly 456 diverse conditions for most of the magma reservoir's lifetime, varying between hot, 457 titanite-undersaturated and, more commonly, near-solidus, titanite-saturated (< 734 °C) 458 melts. This is consistent with previous results for KNT implying magma storage 459 dominantly within the titanite crystallisation window (Szymanowski et al., 2017) as well 460 as thermal models (Gelman et al., 2013; Karakas et al., 2017) suggesting that maintaining 461 upper-crustal silicic magma reservoirs for 10^5 – 10^6 years is favoured for high-crystallinity, 462 near-solidus bodies that receive their heat through episodic magma recharge (here likely 463 represented by 'hot', high-REE, high-Eu/Eu* melts). We interpret the last ~50 ky to 464 represent a period of increased recharge heat and mass supply which resulted in decrease 465 in crystallinity, increase in temperature and gradual homogenisation of the magma 466 reservoir in the lead-up to eruption (Fig. 9). Similar mechanisms have been invoked as 467 means of rejuvenating evolved magmatic systems from their baseline, high-crystallinity 468 state to an intermediate-crystallinity state that is rheologically mobile and eruptible, with 469 modelled timescales between months to years (Burgisser and Bergantz, 2011) to 10^3-10^5 470 years (Bachmann and Bergantz, 2003; Huber et al., 2012). Other studies using zircon 471 geochronology have inferred timescales of ~200 ky for the 5000 km³ Fish Canyon Tuff 472 (Wotzlaw et al., 2013), ~10 ky for the 1000 km³ Lava Creek Tuff (Matthews et al., 2015), 473 ~15-40 ky for smaller eruptions at Soufrière, St. Lucia (Barboni et al., 2016). Here we 474 show that for the >900 km³ Kneeling Nun Tuff, rejuvenation took on the order of 50 ky, 475 which adds to the growing database of such well-described eruptive units. 476

477 6.3. Coeval environments of variable cooling history

Studying clasts erupted together with the KNT ignimbrite allows us to evaluate not only 478 the homogeneity of the system in major and trace element compositions (section 6.1) but 479 also its temporal evolution across multiple 'facies' of the magmatic source. The fact that 480 there is no clear distinction in the mineral compositions between these clasts 481 (Supplementary Fig. 4), as well as the great overlap in zircon dates (Fig. 5) and trace 482 elements (Fig. 6), show that all these lithologies are sampled from the same, voluminous, 483 long-lived (> 1 My) upper-crustal magma reservoir. However, the textures of the clasts 484 485 (Fig. 2) suggest different scenarios for their final cooling and solidification, ranging from slow cooling for the holocrystalline, plutonic samples, to rapid but sub-surface freezing 486 of the porphyritic clasts and syn-eruptive quenching of the pumices. The textural 487 information is aided by zircon age distributions (Fig. 5), creating a fingerprint of the 488 thermal history of individual magma volumes in the context of the entire magma 489 reservoir (Fig. 9). The plutonic clasts likely represent peripheral volumes of the system; 490 we speculate that at some point of its maturation, insufficient heat is supplied from the 491 recharging magma to keep the particular magma portion above solidus, resulting in slow 492 493 cooling and formation of the plutonic rind (effectively the wall rock) of the system. Porphyritic clasts require rapid freezing, which may be a result of decompression, e.g. 494 related to previous eruptions (such as the Sugarlump tuffs), or ascent and emplacement in 495 much cooler surroundings. Long apparent hiatuses in zircon crystallisation (such as 280 496 ky in porphyritic clast 1509A; Fig. 5) suggest locally or episodically slowed growth rates 497 or zircon undersaturation and resorption; however, they do not require extended 498 subsolidus storage. Finally, pumices represent batches of magma that was mobile at 499 eruption (Fig. 9). Irrespective of the complexity of individual cooling paths of the clasts, 500 501 the reproducibility of the age spectrum of the bulk ignimbrite sample in the clast-hosted zircons (Fig. 5) suggests that every sample may capture essentially the entire life of the 502 KNT magmatic system from early intrusions to solidification/eruption. 503

504 6.4. Zircon age distributions and the estimation of eruption ages

505	Dating past eruptions is an invaluable component of many studies requiring independent
506	information about the timing of events in the geological past. Indeed, ID-TIMS U-Pb
507	dating of zircon from distal volcanic ash beds intercalated with sedimentary sequences
508	has played a key role in the establishment of the absolute time framework of the geologic
509	timescale (Gradstein et al., 2012). Understanding magmatic zircon age distributions and
510	developing accurate ways of estimating the eruption age from a population of volcanic
511	zircon (see e.g. Schmitz and Davydov, 2011; Schoene et al., 2015; Keller et al., 2018 for
512	interpretation strategies) is therefore critical to progress in resolving the rates of
513	geological processes. The large (n=76) set of ID-TIMS dates generated here from a
514	proximal deposit of a super-eruption (Fig. 5) can be considered a suitable proxy for the
515	true distribution of zircon crystallisation ages in upper-crustal magma bodies (albeit one
516	truncated at eruption).

A key observation that can be made for KNT zircon is that their distribution in time (and 517 518 temperature; Figs 5, 6) differs from distributions predicted by theoretical considerations or observed in simple plutonic systems (Watson, 1996; Samperton et al., 2017; Keller et 519 al., 2018). In particular, the main apparent peak of zircon crystallisation occurs relatively 520 late in the total lifetime of the system, some 100–300 ky before the eruption (Fig. 5). 521 While our dataset might to some extent be biased by high U contents (pulling the grain-522 average ages towards times of crystallisation from high-crystallinity, evolved magma), it 523 should be expected that incrementally built magma reservoirs characterised by protracted 524 growth and storage have a history involving multiple transitions between zircon-saturated 525 and undersaturated conditions. Consequently, models proposing a simple relationship 526 between temperature, time and zircon saturation (Samperton et al., 2017) can only work 527 for the simplest of systems such as monotonously cooled, single magma batches. We 528

expect the products of most (at least wet, calc-alkaline) explosive volcanic eruptions of
all but the smallest size to have complex zircon age spectra such as that shown here for
KNT.

In cases where the total timescale of zircon crystallisation is much greater than analytical uncertainty (such as the KNT), both youngest-zircon and Bayesian modelling approaches to eruption age estimation can be expected to give indistinguishable and accurate results for all reasonable zircon numbers (n > ca. 10-15) (Keller et al., 2018). However,

strategies for estimating eruption ages of many other, particularly ash bed, samples (other 536 537 n, absolute age, analytical uncertainty, age dispersion) might benefit from directed rather than random sampling, e.g. using additional textural and compositional information from 538 the available zircons. Our data show that KNT zircons younger than ~35.35 Ma, i.e. those 539 540 interpreted to represent the rejuvenation interval, are distinct both texturally (large, CLbright, simple zoning; Fig. 4) and compositionally (low REE, high Eu/Eu*, Ti; Fig. 6). If 541 such systematics are widespread in explosive volcanic units, then age interpretations can 542 be substantially improved by careful characterisation of ash bed zircons with either in situ 543 or bulk analyses (Schoene et al., 2010; Schoene et al., 2015; Wotzlaw et al., 2018). 544 545 Gathering compositional information from zircons from out-of-context or altered airfall ash beds (bentonites, tonsteins etc.) can have the additional benefit of establishing the 546 tectonic affinity of the source of volcanism (e.g. Grimes et al., 2015), which should 547 548 further improve the age interpretations as age dispersion may be systematically different for within-plate and subduction volcanism. 549

550 **7. Conclusions**

Zircon age and trace element data presented here for the Kneeling Nun magmatic system
 provide a detailed record of magma chamber maturation and rejuvenation in the build-up

to one of the largest eruptions in the geological record. This unique, large dataset for a 553 single eruption reveals long and complex storage of magma in the form of a high 554 crystallinity mush, dominantly at near-solidus temperatures (< ca. 730 °C), but large 555 internal temperature and crystallinity variations as a function of location with respect to 556 the heat source. We show that the prolonged accumulation, storage and maturation of 557 KNT magmas of at least 1.5 million years culminated in a period of ~50 ky of increase in 558 heat supply and related homogenisation, decrease in crystallinity, reversal in the degree of 559 560 melt evolution and, potentially, increase in average melt temperature. The decrease in crystallinity in particular may have conditioned the magmatic system for the cataclysmic 561 eruption by driving it from rheologically immobile to mobile conditions; however, with 562 our data we cannot address the ultimate eruption trigger. The insights gained from the 563 zircon record, aided by estimates of magma storage conditions from major mineral 564 phases, make the Kneeling Nun Tuff an extraordinary subject to develop new ways of 565 studying the pre-eruptive history of magmas. 566

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575 Figure captions

Fig. 1. Location of the study area and Kneeling Nun Tuff sampling sites. (a) Map of the 576 distribution of Tertiary volcanic rocks in SW North America (modified from McDowell 577 and McIntosh, 2012); SJ-San Juan/Southern Rocky Mountain volcanic field; MD-578 579 Mogollon-Datil; BH-Boot Heel; TP-Trans-Pecos; SMO-Sierra Madre Occidental; GB-Great Basin. (b) Location of the Emory caldera, source of the Kneeling Nun Tuff, within 580 the Mogollon-Datil volcanic field in western New Mexico, with the approximate extent 581 of the KNT ignimbrite sheet proposed by McIntosh et al. (1992) based on paleomagnetic 582 and ⁴⁰Ar/³⁹Ar data of distal samples. Three key areas were targeted for sampling: western 583 outflow sheet at Lucky Bill Canyon, Hurley and inside Chino Mine; intracaldera KNT 584 along NM-152 west of Emory Pass; eastern outflow sheet immediately south of Tierra 585 Blanca valley. 586 Fig. 2. Field appearance and microscopic textures of studied lithologies. (a) The eruptive 587 unit's namesake, the Kneeling Nun landmark near Santa Rita, NM. (b-f) Field 588 appearance of studied clasts including crystal-rich pumice (b), plutonic clasts (c,f) and 589 porphyries (d,e). The field scale in d is marked every 1 cm. (g-j) Cross-polarised light 590 thin section images of representative samples of a porphyry (1509A, g), a crystal-rich 591

⁵⁹² pumice (1525-2, **h**), an evolved, quartz-rich pumice (1434, **i**) and a holocrystalline

⁵⁹³ granitic clast (1421, **j**).

Fig. 3. Trace element (Ba, Sr) compositions of representative KNT sanidine, illustrating
the magnitude of variations in compatible elements. Inset: a backscattered electron image
of a sanidine crystal typical for late-erupted material (Table 1) with a prominent, high-Ba
rim.

Fig. 4. Cathodoluminescence (CL) images of representative Kneeling Nun Tuff zircon 598 crystals from samples 1402, 1416, 1509A, 1511, and 1525-2. Note the frequent 599 truncations and complex zonation patterns. The white frame highlights CL-bright, simply 600 zoned, REE-depleted crystals with ²⁰⁶Pb/²³⁸U dates between 35.352 and 35.305 Ma. 601 Fig. 5. Texturally resolved geochronology of the Kneeling Nun magmatic system. 602 Coloured bars represent Th-corrected ID-TIMS ²⁰⁶Pb/²³⁸U dates of individual zircon 603 crystals together with their 2σ uncertainty. Bulk-ignimbrite zircon and titanite data for 604 sample 1402 is reproduced from Szymanowski et al. (2017). ⁴⁰Ar/³⁹Ar sanidine dates for 605 KNT and uppermost Sugarlump tuffs (McIntosh et al., 1990) were recalculated to the 606 calibration of Kuiper et al. (2008). The preferred eruption age is the Bayesian estimate 607 following Keller et al. (2018) displayed with three uncertainty envelopes: internal 608 only/with tracer calibration/with tracer and ²³⁸U decay constant. Side panel: colour-coded 609 kernel density plots illustrating the zircon age distribution of individual samples and a 610 histogram of all zircon dates in this study. 611

Fig. 6. Variability of selected trace elements in Kneeling Nun Tuff zircon through time. 612 Each point represents one in situ LA-ICPMS analysis prior to ID-TIMS U-Pb dating of 613 the bulk crystal; in cases where multiple spot analyses of a crystal are available, they are 614 assigned the same crystallisation age. Note that the real crystallisation ages of the 615 sampled spots may deviate from the assigned ones as bulk U-Pb dates are likely to be 616 biased towards ages of rims and high-U zones. Box plots show medians, interquartile 617 ranges (IR), and extreme values for bins of 50 ky (7 youngest bins) or more (dates > 618 35.655 Ma). T-tests for Eu/Eu* (a) and Ti (b) reveal that compositions of zircon in the 619 youngest bin (50 ky prior to eruption, grey shaded area) are statistically distinct from the 620 compositions of older crystals at high significance level (p < 0.01). These younger 621 crystals further show significantly lower variance with respect to Dy and Yb/Dy. Typical 622

uncertainties are based on counting statistics for element ratios (Yb/Dy, Eu/Eu*) or 623 counting statistics and the composition of primary reference materials for Ti and Dy. For 624 Dy the error bar is smaller than symbol size. Ti was either analysed relative to reference 625 zircon GZ7 (Szymanowski et al., 2018) for clast-hosted zircon or recalculated to match 626 the same calibration (via zircon 91500) for previously analysed zircon from bulk sample 627 1402. Ti-in-zircon temperature estimates use the model of Ferry and Watson (2007) and 628 assume same activity values as in Szymanowski et al. (2017). 629 Fig. 7. Trace elements in zircon and their corresponding melts, colour-coded for Ti 630 631 content in zircon. (a) Results of LA-ICPMS measurements of KNT zircon across all dated samples. (b) Melts in equilibrium with individual measured zircon compositions, 632 calculated using power-law fits between Ti and zircon-melt partition coefficients 633 (Claiborne et al., 2018). Titanite saturation temperature is the average Zr-in-titanite 634 temperature of Szymanowski et al. (2017) adjusted for pressure of 2.2 kbar. 635 Fig. 8. Composition of reconstructed Kneeling Nun Tuff melts through time. Each point 636 637 corresponds to a datum in Fig. 6. The time coordinate is identical to that of the corresponding whole-zircon crystallisation age, while the composition is recalculated 638 from the respective *in situ* zircon analysis using the model of Claiborne et al. (2018) as in 639 Fig. 7. In cases of multiple compositions assigned to the same age, the points are 640 connected with a vertical line. 641 Fig. 9. Conceptual model of the storage and remobilisation of the Kneeling Nun 642 magmatic system. (a-b) Two key stages of evolution of the magma reservoir prior to 643 eruption: long-term mush residence (a) and pre-eruptive remobilisation (b). Coloured 644 circles correspond to locations of the magmatic clast samples. For most of the reservoir's 645 lifetime (a), magma is stored at high but variable crystallinity depending on proximity to 646 the recharge heat source. Most of the magma volume is stored as immobile, rigid crystal

647

648	framework ('mush', $>$ ca. 50% crystals) below titanite saturation (T ttn \sim 730 °C).
649	Locally, pools of evolved melt may form by extraction from the crystal framework.
650	Where the amount of supplied heat is insufficient, magma solidifies to form the plutonic
651	rind of the system. (b) In the last ca. 50 ky prior to eruption, an increase in recharge rate
652	results in a gradual, large-scale decrease in crystallinity (to about 40–50%, i.e. eruptible
653	state), which may facilitate homogenisation by overturn. The ultimately erupted material
654	is a mixture of different environments within the magma reservoir, volumetrically
655	dominated by the mush zone, with a minor proportion of extracted melts. (c) A schematic
656	depiction of the temperature evolution of the KNT reservoir, with temperature cycling as
657	a function of recharge. Individual clasts sample the same maturation history but differ in
658	the time and mode of final cooling, from early solidification of some porphyry and
659	plutonic lithologies to quenching upon eruption for the pumices.
660	

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Fig. 1. Location of the study area and Kneeling Nun Tuff sampling sites. (**a**) Map of the distribution of Tertiary volcanic rocks in SW North America (modified from McDowell and McIntosh, 2012); SJ–San Juan/Southern Rocky Mountain volcanic field; MD–Mogollon–Datil; BH–Boot Heel; TP–Trans-Pecos; SMO–Sierra Madre Occidental; GB–Great Basin. (**b**) Location of the Emory caldera, source of the Kneeling Nun Tuff, within the Mogollon–Datil volcanic field in western New Mexico, with the approximate extent of the KNT ignimbrite sheet proposed by McIntosh et al. (1992) based on paleomagnetic and ⁴⁰Ar/³⁹Ar data of distal samples. Three key areas were targeted for sampling: western outflow sheet at Lucky Bill Canyon, Hurley and inside Chino Mine; intracaldera KNT along NM-152 west of Emory Pass; eastern outflow sheet immediately south of Tierra Blanca valley.



Fig. 2. Field appearance and microscopic textures of studied lithologies. (a) The eruptive unit's namesake, the Kneeling Nun landmark near Santa Rita, NM. (**b-f**) Field appearance of studied clasts including crystal-rich pumice (**b**), plutonic clasts (**c**,**f**) and porphyries (**d**,**e**). The field scale in d is marked every 1 cm. (**g-j**) Cross-polarised light thin section images of representative samples of a porphyry (1509A, **g**), a crystal-rich pumice (1525-2, **h**), an evolved quartz-rich pumice (1434, **i**) and a holocrystalline granitic clast (1421, **j**).



Fig. 3. Trace element (Ba, Sr) compositions of representative KNT sanidine, illustrating the magnitude of variations in compatible elements. Inset: a backscattered electron image of a sanidine crystal typical for late-erupted material (Table 1) with a prominent high-Ba rim.



Fig. 4. Cathodoluminescence (CL) images of representative Kneeling Nun Tuff zircon crystals from samples 1402, 1416, 1509A, 1511, and 1525-2. Note the frequent truncations and complex zonation patterns. The white frame highlights CL-bright, simply zoned, REE-depleted crystals with ²⁰⁶Pb/²³⁸U dates between 35.352 and 35.305 Ma.



Fig. 5. Texturally resolved geochronology of the Kneeling Nun magmatic system. Coloured bars represent Th-corrected ID-TIMS ²⁰⁶Pb/²³⁸U dates of individual zircon crystals together with their 2σ uncertainty. Bulk-ignimbrite zircon and titanite data for sample 1402 is reproduced from Szymanowski et al. (2017). ⁴⁰Ar/³⁹Ar sanidine dates for KNT and uppermost Sugarlump tuffs (McIntosh et al., 1990) were recalculated to the calibration of Kuiper et al. (2008). The preferred eruption age is the Bayesian estimate following Keller et al. (2018) displayed with three uncertainty envelopes: internal only/with tracer calibration/with tracer and ²³⁸U decay constant. Side panel: colour-coded kernel density plots illustrating the zircon age distribution of individual samples and a histogram of all zircon dates in this study.



Fig. 6. Variability of selected trace elements in Kneeling Nun Tuff zircon through time. Each point represents one in situ LA-ICPMS analysis prior to ID-TIMS U–Pb dating of the bulk crystal; in cases where multiple spot analyses of a crystal are available, they are assigned the same crystallisation age. Note that the real crystallisation ages of the sampled spots may deviate from the assigned ones as bulk U–Pb dates are likely to be biased towards ages of rims and high-U zones. Box plots show medians, interquartile ranges (IR), and extreme values for bins of 50 ky (7 youngest bins) or more (dates > 35.655 Ma). T-tests for Eu/Eu* (**a**) and Ti (**b**) reveal that compositions of zircon in the youngest bin (50 ky prior to eruption, grey shaded area) are statistically distinct from the compositions of older crystals at high significance level (p < 0.01). These younger crystals further show significantly lower variance with respect to Dy and Yb/Dy. Typical uncertainties are based on counting statistics for element ratios (Yb/Dy, Eu/Eu*) or counting statistics and the composition of primary reference materials for Ti and Dy. For Dy the error bar is smaller than symbol size. Ti was either analysed relative to reference zircon GZ7 (Szymanowski et al., 2018) for clast-hosted zircon or recalculated to match the same calibration (via zircon 91500) for previously analysed zircon from bulk sample 1402. Ti-in-zircon temperature estimates use the model of Ferry and Watson (2007).



Fig. 7. Trace elements in zircon and their corresponding melts, colour-coded for Ti content in zircon. (**a**) Results of LA-ICPMS measurements of KNT zircon across all dated samples. (**b**) Melts in equilibrium with individual measured zircon compositions, calculated using power-law fits between Ti and zircon-melt partition coefficients (Claiborne et al., 2018). Titanite saturation temperature is the average Zr-in-titanite temperature of Szymanowski et al. (2017) adjusted for pressure of 2.2 kbar.



Fig. 8. Composition of reconstructed Kneeling Nun Tuff melts through time. Each point corresponds to a datum in Fig. 6. The time coordinate is identical to that of the corresponding whole-zircon crystallisation age, while the composition is recalculated from the respective in situ zircon analysis using the model of Claiborne et al. (2018) as in Fig. 7. In cases of multiple compositions assigned to the same age, the points are connected with a vertical line.



Fig. 9. Conceptual model of the storage and remobilisation of the Kneeling Nun magmatic system. (**a-b**) Two key stages of evolution of the magma reservoir prior to eruption: long-term mush residence (**a**) and pre-eruptive remobilisation (**b**). Coloured circles correspond to locations of the magmatic clast samples. For most of the reservoir's lifetime (**a**), magma is stored at high but variable crystallinity depending on proximity to the recharge heat source. Most of the magma volume is stored as immobile, rigid crystal framework ('mush', > ca. 50% crystals) below titanite saturation (T ttn ~ 730 °C). Locally, pools of evolved melt may form by extraction from the crystal framework. Where the amount of supplied heat is insufficient, magma solidifies to form the plutonic rind of the system. (**b**) In the last ca. 50 ky prior to eruption, an increase in recharge rate results in a gradual, large-scale decrease in crystallinity (to about 40–50%, i.e. eruptible state), which may facilitate homogenisation by overturn. The ultimately erupted material is a mixture of different environments within the magma reservoir, volumetrically dominated by the mush zone, with a minor proportion of extracted melts. (**c**) A schematic depiction of the temperature evolution of the KNT reservoir, with temperature cycling as a function of recharge. Individual clasts sample the same maturation history but differ in the time and mode of final cooling, from early solidification of some porphyry and plutonic lithologies to quenching upon eruption for the pumices.

Table 1

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Summary of crystallinities, compositions and intensive parameters calculated for key samples of Kneeling Nun Tuff and its magmatic clasts.

Sample	crystallinity [%] ^a	SiO ₂ [wt%] ^b	plagioclase An °	sanidine Or °	high-Ba rims	two-feldspar T [°C] ^{cd}	amphibole– plagioclase T [°C] °	amphibole P [kbar] ^{fg}
bulk ignimb	rite							
1519	11		13–16	69–71		640–689		
1520	58	76.9	13–23	63–65		697–762		
1521	32	72.9	14–27	62–65		718–785		
1522	49	69.0	20-28	61–64	х	767–823	744-803	2.21 ± 0.13
1402	46	69.5	21-28	61–66	х	729–822	746-801	2.21 ± 0.09
1523	55	67.1	21-27	61–64	х	765-833		
1428	32	75.8	11–23	61–65		675–763		
1430	48	75.1	19–23	62–65	х	747–777		
1435	44	75.7	20–23	59–64	х	722-810		
pumices								
1434A	26	77.1	14–19	62–65		700–728		
1525-2	46	70.3	20-27	62–64	х	757–849	757-810	2.19 ± 0.09
porphyrytic	clasts							
1416A	56	73.8	18–24	64–68		729–780		
1509A	60	67.9	20-27	65–69	х	709-800	754-808	2.25 ± 0.16
1511	62	69.0	22–26	66–68	х	727–797	761-800	2.22 ± 0.09
plutonic clasts								
1421	100	75.6	15-22	61–63		695–740		
1510	100	77.0	16–19	61–62		684–750		

^a crystallinity determined by point counting

 $^{\rm b}\,{\rm SiO}_2$ from XRF analyses, all major elements normalised to 100% on anhydrous basis

° excluding outliers as defined in Supplementary Fig. 4

^d equation 27b of Putirka (2008)

^e thermometer B of Holland and Blundy (1994)

^f Mutch et al. (2016)

^g reported uncertainty (1s) is a function of the scatter of Al tot in amphibole; the uncertainty of the thermometer calibration is ca. 0.4 kbar