

ZIRCON AS A PROVENANCE TRACER: COUPLING RAMAN SPECTROSCOPY AND U-Pb GEOCHRONOLOGY IN SOURCE-TO-SINK STUDIES

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ABSTRACT

U-Pb zircon geochronology is one of the most widely used techniques in sedimentary provenance analysis. Unfortunately, the ability of this method to identify sediment sources is often degraded by sediment recycling and mixing of detritus from different source rocks sharing similar age signatures. These processes create non-unique zircon U-Pb age signatures and thereby obscure the provenance signal. We here address this problem by combining detrital zircon U-Pb geochronology with Raman spectroscopy. The position and width of the Raman signal in zircon scales with its degree of metamictization, which in turn is sensitive to temperature. Thus, combined U-Pb + Raman datasets encode information about the crystallisation history of detrital zircons as well as their thermal history. Using three borehole samples from Mozambique as part of a source-to-sink study of interest for hydrocarbon exploration, we show that zircon populations with similar U-Pb age distributions can exhibit different Raman signatures. The joint U-Pb + Raman analysis allowed us to identify three different annealing trends, which were linked to specific thermal events. Thus we were able to differentiate a dominant Pan-African U-Pb age peak into several sub-populations and highlight the major effect of Karoo tectono-magmatic events. In our case study, we used Raman

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also as a means to systematically identify all zircon grains in heavy-mineral mounts, resulting in considerable time savings. Raman spectroscopy is a non-destructive and cost-effective method that is easily integrated in the zircon U-Pb dating workflow to augment the resolution power of detrital zircon U-Pb geochronology.

Key words: Provenance analysis; U-Pb zircon geochronology; Raman Spectroscopy; Zircon metamictization; Hydrocarbon exploration; Mozambique.

Highlights:

- Raman spectroscopy supplements U-Pb geochronological analysis of detrital zircon
- Thermal overprints revealed by the diverse metamict states of zircon crystals
- New approach allows discrimination of source rocks with same age of crustal growth

1. Introduction

In an era of great improvement of data-acquisition techniques, zircon geochronology is playing a key role in the renewed interest and success of detrital studies (e.g., [Zimmermann et al., 2018](#)). Large sets of reliable U-Pb zircon ages are now rapidly obtained at a reasonable cost and with continuously enhanced efficiency, thus allowing provenance analysis to enter a new era of “big data” ([Vermeesch and Garzanti, 2015](#)).

Zircon, a common accessory component in magmatic and metamorphic rocks, is particularly valuable in the study of sand and sandstone owing to its durability among detrital minerals ([Velbel, 1999](#); [Fedo et al., 2003](#)). In source-to-sink studies, zircon U-Pb data are widely used as a “barcode” fingerprint to be compared with the age signature of the potential sediment sources ([Condie et al., 2009](#); [Gehrels, 2011](#)). The reliability of provenance inferences based on zircon-age fingerprinting, however, is strictly dependent on the existence of source-rock domains characterized by well-defined U-Pb ages. If the potential sources show broad and partially overlapping age spectra, then zircon ages lose much of their discrimination power. Nonetheless, the amount of information that can be extracted from zircon grains is not limited to U-Pb ages, but includes geochemical tracers (e.g., REE or other trace elements; [Hoskin and Ireland, 2000](#)), isotopic tracers (e.g., hafnium and oxygen; [Kemp et al., 2006](#)), fission tracks ([Hurford and Carter, 1991](#)), U-Th/He dating ([Farley, 2002](#)), and zircon typology ([Pupin, 1980](#)). Because of the high content of uranium and thorium (up to 4000 ppm), zircon is on the one hand the ideal target for several dating techniques but on the other hand its crystalline structure is prone to progressive amorphization, owing to accumulation of structural defects induced by recoiling nuclei produced during α -emission events ([Ewing et al., 1987](#); [Weber et al., 1994](#)). The metamictization process induces a physical transformation of zircon crystals with reduction in density and birefringence, decrease in the elastic moduli and Poisson’s ratio, darkening of colour, decrease in hardness, and increase in OH content (e.g., [Holland and Gottfried, 1955](#); [Chakoumakos et al., 1987](#)). The transformation from crystalline to amorphous

27 zircon is a reversible process by subsequent heating, which may eventually lead to annealing and
1 restoration of the crystalline structure (Geisler, 2002). The metamict state of zircon grains thus
28 depends on both actinide content and thermal history (Ginster et al., 2019).
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The degree of metamictization of zircons can be quantified by Raman spectroscopy (Nasdala et al.,
1998, 2001; Zhang et al., 2000), which represents a potentially powerful tool to be applied in
advanced provenance analysis. The treasure of information encrypted in the structure and chemical
composition of zircon crystals can thus be profitably retrieved by combining classical U-Pb dating
with the non-destructive Raman technique.

This article defines a protocol designed in a source-to-sink study of interest for hydrocarbon
exploration in an area of southeastern Africa where Archean cratons and Proterozoic mobile belts
have recorded different and complex thermal histories associated with a series of major magmatic
events. As an example, we use here three core samples from the Cretaceous sedimentary succession
of the Zambezi Delta in central Mozambique. By combining the Raman spectrum of each zircon
grain with its U/Pb age, we could single out detrital subpopulations distinguished not only by their
age but also by their thermal overprint. This new approach represents a promising step forward in
zircon-based provenance analysis.

2. Radiation-induced damage and annealing of zircon lattice

Metamict substances were recognized by Brøgger (1896) as a new class of amorphous matter
previously classified as “hyaline” or “porodine” (i.e., amorphous substances that were originally
crystalline). Accumulation of damage to the crystal structure by the decay of radioactive actinides is
considered the main cause of metamictization in U and Th-bearing minerals (e.g., zircon and
monazite). Decay events produce α particles that move through the crystalline structure and create
several thousand atomic displacements (Murakami et al., 1991).

52 Different stages of metamictization resulting from damage accumulation have been observed in
 1 zircon crystals. In ~570 Ma old natural zircons from Sri Lanka (Murakami et al., 1991), low
 23 radiation doses ($<3 \cdot 10^{15}$ α -events/mg) were observed to produce punctual defects and isolated
 4 distortions in the crystal lattice, whereas with higher doses ($3-9 \cdot 10^{15}$ α -events/mg) only distorted
 54 crystalline domains remained randomly distributed in an amorphous matrix. At highest doses ($\geq 1 \cdot$
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 75 10^{16} α -events/mg), zircon becomes amorphous. While damage is being accumulated in the zircon
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 9 lattice, the annealing process competes to restore crystallinity. When annealing rate exceeds the rate
 106 of damage accumulation, defects are progressively amended (Geisler, 2002).
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16 The annealing process is strongly temperature dependent. Metamict zircon can be annealed to
 17 crystalline state by heating in furnaces for a few hours at ~900 °C (Zhang et al., 2000).
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21 Uncertainties arise when considering annealing over geological times. Metzger and Krogstad (1997)
 22 argued that metamict zircons are completely recovered under metamorphic conditions at 600-650
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 2562 °C, whereas the annealing rate at surface temperature is virtually zero (Hurley and Fairbairn, 1953).
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28 Like damage accumulation, the annealing process proceeds step by step, depending on the initial
 29 degree of metamictization. Fully metamict amorphous zircon anneals only marginally (Murakami et
 30 al., 1991), whereas for partially metamict zircon two-to-three stages of progressive annealing are
 31 necessary (Zhang et al., 2000; Geisler, 2002). Although the evolution of the annealing process is
 32 controversial (Nasdala et al., 2001), this study is based on the widely accepted concept that damage
 33 recovery operates through successive steps and at different rates chiefly controlled by temperature
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48 2.1. Zircon metamict state determined by Raman spectroscopy

49 Together with X-ray diffraction, infrared spectroscopy, electron microprobe and TEM analysis,
 50 Raman spectroscopy has long been established as a suitable means to evaluate the degree of zircon
 51 metamictization (Nasdala et al., 1998, 2001). As radiation damage increases, because of variations
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in bond length and angles, all main Raman peaks progressively broaden, decrease in intensity, and shift towards lower wavenumbers. Among the characteristic Raman peaks, the one related to the Si-O ν_3 stretching band is most sensitive to damage accumulation. Crystalline zircon displays the $\nu_3(\text{SiO}_4)$ Raman peak at $\sim 1008 \text{ cm}^{-1}$ with 5 cm^{-1} full width at half maximum (FWHM). In amorphous zircon, the same Raman peak occurs at $< 955 \text{ cm}^{-1}$ with $\text{FWHM} > 30 \text{ cm}^{-1}$.

These main features of the $\nu_3(\text{SiO}_4)$ Raman peak allow distinction of three classes of zircons based on their metamict state (Zhang et al., 2000; Nasdala et al., 1998): a) crystalline-to-slightly-metamict zircon with peak at $1008\text{--}1000 \text{ cm}^{-1}$ and $\text{FWHM } 5\text{--}10 \text{ cm}^{-1}$; b) metamict zircons with peak at $1000\text{--}990$ and $\text{FWHM } 10\text{--}20 \text{ cm}^{-1}$; c) fully metamict zircons with peak at $990\text{--}955$ and $\text{FWHM } 20\text{--}30 \text{ cm}^{-1}$ (Fig. 1). Because the final metamict state of zircon crystals depends on both accumulated radiation dose and thermal annealing, the relationship between the characteristics of the $\nu_3(\text{SiO}_4)$ Raman peak and the α -dose is generally complex. A linear relationship between the accumulated dose and the FWHM was obtained by Nasdala et al. (2001) for crystalline to moderately metamict zircons not involved in thermal events after crystallization (Fig. 1).

3. Geology of Southern Africa

The Archean core of southern Africa includes the Zimbabwe Craton, comprising a central terrane flanked by two distinct 2.7 Ga greenstone belts (Fig. 2). The central terrane includes 3.5-2.95 Ga gneisses and possibly older greenstone belts, non conformably overlain by 2.9-2.8 Ga volcanic rocks and conglomerates or by a SE-ward thickening 3.0-2.7 Ga sedimentary succession. The craton was stabilized between 2.7 and 2.6 Ga and eventually intruded by the Great Dyke swarm at 2575 Ma (Jelsma and Dirks, 2002). The craton grew progressively during the Paleoproterozoic and Mesoproterozoic (Jacobs et al., 2008), and was affected by intraplate magmatism at 1.4-1.35 Ga in the south, and next again at 1.1 Ga (Hanson et al., 2006).

103 Orogens formed during the Mesoproterozoic include the Irumide Belt, extending from central
104 Zambia in the SW to northern Malawi in the NE, delimited by the largely undeformed basement of
105 the Bangweulu block in the NW, and largely affected by the Neoproterozoic orogeny in the west
106 and southwest. The Irumide Belt includes granitoid suites emplaced between 1.65 and 1.55 Ga,
107 between 1.36 and 1.33 Ga only in the NE, and between 1.05 and 0.95 Ga, together with siliciclastic
108 and minor carbonate rocks deposited around 1.85 Ga. The metamorphic grade increases from
109 greenschist facies in the NW (1.02 Ga) to upper amphibolite facies in the SE (1.05 Ga; [De Waele et al., 2006](#)). The Choma–Kalomo block in southern Zambia is a distinct Mesoproterozoic domain also
110 including granitoid intrusions and amphibolite-facies metasediments affected by a thermal event
111 between 1020 and 980 Ma ([Glynn et al., 2017](#)).

112 The major Neoproterozoic Pan-African orogeny is represented by the Damara–Lufilian–Zambezi
113 belt, which stretches from coastal Namibia in the west and across Botswana and southern Zambia to
114 finally connect with the Mozambique Belt in the east ([Goscombe et al., 2019](#)). The Zambezi Belt
115 contains a volcano-sedimentary succession deformed under amphibolite-facies conditions at 0.9-0.8
116 Ga ([Hanson, 2003](#)), whereas eclogite-facies metamorphism dated at 592 Ma constrains the timing
117 of subduction with subsequent thrust emplacement dated as 550-530 Ma ([Hargrove et al., 2003](#)).

118 The several km-thick Karoo Supergroup, including upper Paleozoic glacial sediments, shales and
119 volcanoclastic sandstones followed by quartzo-feldspatho-lithic fluvial sediments in the Triassic,
120 was widely deposited across southern Africa ([Johnson et al., 1996](#); [Catuneanu et al., 2005](#)). Karoo
121 sedimentation was terminated by flood-basalt eruptions recorded at ~180 Ma ([Svensen et al., 2012](#)).

122 Rifting and break-up of Gondwana finally led to opening of the Indian Ocean in the Early
123 Cretaceous, an event associated with extensive volcanism in the Mozambique channel ([König and
124 Jokat, 2010](#)). Inland, fluvial and lacustrine sediments were deposited in the Kalahari basin during
125 the Cenozoic, reworked by eolian activity during Quaternary dry stages ([Haddon and McCarthy,
126 2005](#)).

129 3.1. Core stratigraphy

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The studied core is located in the Zambezi Delta region of central Mozambique. The Lower Cretaceous succession includes over 1 km-thick mudrocks with interbedded fine-grained feldspatho-quartzo-lithic to medium-grained feldspatho-litho-quartzose sandstones (Lower Lupata Fm.; [Salman and Abdula, 1995](#)). Sandstones include monocrystalline quartz with rounded to subrounded outline and abraded overgrowths and felsic volcanic to subvolcanic grains locally containing quartz phenocrysts (sample NH45, age: Valanginian/Hauterivian). Above, the medium to coarse-grained feldspatho-litho-quartzose or litho-feldspatho-quartzose sandstones interbedded in the 652 m-thick Upper Lupata Formation are overlain by a medium-grained feldspatho-quartzo-lithic volcanoclastic sand containing microlitic and felsitic volcanic lithics, and, locally, a few aegirine grains (sample NH27, age: late Aptian/earlyAlbian). The overlying Sena Formation, 2688 m-thick, includes fine to coarse-grained sandstones ranging in composition from quartzo-feldspathic to feldspatho-quartzose (NH10, age: Cenomanian/Turonian). Granitoid rock fragments are common and garnet-bearing micaschist grains occur. Above, the 366 m-thick Upper Cretaceous to Oligocene succession includes fine to medium-grained litho-feldspatho-quartzose sandstones, followed by 219 m-thick, feldspar-rich feldspatho-quartzose to feldspatho-litho-quartzose sandstones of Miocene age.

4. Methods

Zircon grains from the three selected sand-sized samples NH45, NH27, and NH10 were concentrated using standard gravimetric and magnetic techniques. From an aliquot of the 15-500 μm size class obtained by wet sieving, dense minerals were separated in sodium polytungstate ($\rho=2.90 \text{ g/cm}^3$) and recovered after partial freezing with liquid nitrogen. Zircons were concentrated with a Frantz isodynamic magnetic separator. The concentrate, obtained without any additional

155 separation either with denser liquids or by hand-picking to avoid selection bias, was poured on a
1 standard glass slide, impregnated with araldite epoxy, and polished to expose the grain surfaces.

157 A complete photo-mosaic acquired for each slide using a motorized stage and camera was geo-
158 referenced in a GIS environment using a previously defined Cartesian reference system. All grains
159 were outlined by image-segmentation techniques. For each grain, the coordinates of its centroid
160 were calculated, and the corresponding points analysed with a Renishaw InVia™ Raman
161 spectrometer (laser 532 nm; 5 cycles of 0.5 s each; 20x magnification; laser power 30 mW on
162 sample). After baseline correction, the collected spectra were classified based on a reference
163 database, allowing the identification of all zircon grains together with their coordinates for further
164 analyses. One of the advantages of such automated phase mapping (Vermeesch et al., 2017) is that
165 all zircons are picked, including murky grains easily discarded by visual inspection.

166 For each Raman spectrum identified as zircon, the position and width of the diagnostic peaks at
167 202-235, 356, 438, 974, 1008 cm^{-1} (Dawson et al., 1971) were calculated using the peak-fitting
168 algorithm designed for Matlab™ by Tom O'Haver (2020), which uses an unconstrained non-linear
169 optimization algorithm to decompose the Raman spectrum into its component parts. A pseudo-
170 Voigt shape was selected for peak fitting (Fig. 3). The precise position and full widths at half
171 maximum (FWHM) of the $\nu_3(\text{SiO}_4)$ Raman peak located around 1008 cm^{-1} were recorded
172 (Appendix Table A1).

173 U-Pb dating of the same zircon grains analysed by Raman spectroscopy was carried out at the
174 London Geochronology Centre using an Agilent 7700x laser ablation-inductively coupled plasma-
175 mass spectrometry (LA-ICP-MS) system, employing a NewWave NWR193 Excimer Laser
176 operated at 10 Hz with a 20 μm spot size and $\sim 2.5 \text{ J/cm}^2$ fluence. The laser spot was invariably
177 placed in the middle of zircon grains in the same place analysed by Raman spectroscopy. The mass
178 spectrometer data were converted to isotopic ratios using GLITTER 4.4.2 software (Griffin et al.,
179 2008), employing Plešovice zircon (Sláma et al., 2008) as a primary age standard and GJ-1 (Jackson
180 et al., 2004) as a secondary age standard. NIST SRM612 was used as a compositional standard for

181 the U and Th concentrations. We used $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ages for zircons younger and older
 182 than 1100 Ma, respectively. No common Pb correction was applied. Grains with $> +5/-15\%$ age
 183 discordance were discarded.

184 For each dated grain, the alpha-decay dose was calculated according to [Condon et al. \(2015\)](#)
 185 assuming a concentration of $^{235}\text{U} \approx 1/137.818 \text{ } ^{238}\text{U}$:

$$(1) \quad \text{dose} = 8[^{238}\text{U}]e^{(238\text{U}\lambda \times \text{age})-1} + 7[^{235}\text{U}]e^{(235\text{U}\lambda \times \text{age})-1} + 6[^{232}\text{Th}]e^{(232\text{Th}\lambda \times \text{age})-1} .$$

187 Geochemical and geochronological data, $\nu_3(\text{SiO}_4)$ Raman peak positions and widths, and the
 188 calculated alpha-decay dose for each zircon grain are provided in [Appendix Table A1](#).

190 5. Results

192 The ICP-MS analysis of the studied zircon grains has revealed a rather uniform distribution in
 193 actinide concentration among the samples, with $[^{238}\text{U}]$ ranging from 222 to 3485 ppm and $[\text{Th}]$ from
 194 73 and 2330 ppm (5th and 95th percentiles respectively; [Appendix Table A1](#)). The radiation dose
 195 calculated for each zircon grain based on *equation 1* ranges from $\sim 2.5 \cdot 10^{14}$ to $\sim 1.5 \cdot 10^{16}$ α -
 196 events/mg. Sample NH10 and NH27 display the same range of α -decay events/mg (from $2 \cdot 10^{14}$ to
 197 $1.2 \cdot 10^{16}$), whereas a larger range is obtained for sample NH45 (from $4 \cdot 10^{14}$ to $1.5 \cdot 10^{16}$), where
 198 the highest doses are found. The average doses are similar overall (10^{15}) but increase from sample
 199 NH10 ($2.9 \cdot 10^{15}$) to samples NH27 and NH45 ($\sim 4 \cdot 10^{15}$). The two main age clusters recurring in
 200 the analysed samples are named for simplicity “Irumide” (0.9–1.1 Ga, Tonian to Stenian) and “Pan-
 201 African” (0.5–0.65 Ga, Cambrian to late Neoproterozoic).

203 5.1. U/Pb zircon ages

205 In the three selected samples, 90 to 160 zircon grains have been dated overall, but only grains with
 1 concordant age and for which the Raman spectrum allowed confident determination of the position
 206 and width of the $\nu_3(\text{SiO}_4)$ Raman peak were considered for further analysis (Fig. 4). The U-Pb age
 207 spectrum of detrital zircons from sample NH45 (n = 61) shows prominent Pan-African and Irumide
 208 peaks. The youngest ages form a Permian cluster (259-276 Ma, 7% of total ages), the oldest ages
 209 are Paleoproterozoic (1649-2066 Ma, 5% of total ages).

211 Detrital zircons in sample NH27 (n = 64) yielded clusters of Early Cretaceous (110-118 Ma, 14% of
 212 total ages), Pan-African (17% of total ages), Irumide (31% of total ages) and late Paleoproterozoic
 213 U-Pb ages (1676-2055 Ma, 16% of total ages). One Permian (265 Ma) and one Devonian age (380
 214 Ma) were also obtained. The U-Pb age spectrum of detrital zircons from sample NH10 (n = 134)
 215 displays dominant Pan-African (42% of total ages) and Irumide peaks with one Early Cretaceous
 216 (128 Ma) and three Paleoproterozoic ages (1855-2146 Ma).

218 5.2. Raman analysis

219 From the three selected samples, 259 detrital zircons were analysed considering the position and
 220 width (full width at half maximum – FWHM) of the $\nu_3(\text{SiO}_4)$ Raman peak. The position varies
 221 between 994 and 1008 cm^{-1} , whereas FWHM varies between 5 and 24 cm^{-1} . Most analyzed zircon
 222 grains are crystalline (peak position > 1002 cm^{-1} and width < 10 cm^{-1}), whereas <25% of them show
 223 Raman characteristics typical of metamict grains. Fully metamict amorphous zircons with FWHM
 224 values > 30 cm^{-1} were not detected. Raman scattering results are uniformly distributed among the
 225 three samples irrespective of their stratigraphic position. In all samples, peak positions and FWHM
 226 values display inverse correlation (r -0.90 overall, ranging from -0.87 to -0.92) (Fig. 5) with
 227 mathematical relationship estimated as:

$$229 \quad (2) \quad \nu_3(\text{SiO}_4)\text{peak position} = 1010 * e^{-0.0006209 * \nu_3(\text{SiO}_4)\text{FWHM}}$$

Equation 2 allows us to use the peak position, which is more reproducible and easier to obtain than the commonly used FWHM value (e.g., [Nasdala et al., 2001](#)), as a proxy of zircon metamict state.

6. Discussion

6.1 Relationship between zircon age and metamict state

The accumulated radiation doses are strongly variable within each age population of zircon grains, because they depend not only on the time available for α -decay but also on actinide concentration, which varies over two orders of magnitude. Doses calculated for grains younger than 1.5 Ga cover the entire spectrum from $0.2 \cdot 10^{15}$ up to $1.2 \cdot 10^{16}$ α -events/mg, whereas higher doses characterize only grains older than 1.5 Ga, which never show values lower than $3.5 \cdot 10^{15}$ α -events/mg ([Fig. 6A](#)).

Because the position and width of the $\nu_3(\text{SiO}_4)$ Raman peak are strongly dependent on the metamictic state of zircon grains (and consequently on the accumulated damage by α decay), a correlation between age and Raman peak position (or width) is expected, with oldest zircons characterized by highest doses. However, low positions and large widths of the $\nu_3(\text{SiO}_4)$ Raman peaks are displayed only by zircons dated around 0.1, 0.6, and 1 Ga, whereas older zircons are invariably characterized by rather narrow peaks ([Fig. 6B, 6C](#)). The lack of old metamict zircon grains may have two explanations: a) strongly metamict zircons are prone to chemical dissolution ([Ewing et al., 1982](#); [Balan et al., 2001](#)) and possibly also to mechanical breakdown during sediment transport owing to reduced hardness ([Chakoumakos et al., 1987](#)), and may thus be selectively lost during one or more sedimentary or metamorphic cycles ([Malusà et al., 2013](#); [Garzanti et al., 2019](#)); b) strongly metamict zircons are characterized by such low and wide Raman peaks (fig. 1 in [Zhang et al., 2000](#)) that their identification becomes problematic. In any case, the high crystallinity of even

255 the oldest zircon grains testifies to the role played by subsequent thermal events that induced lattice
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 256 annealing.

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 258 *6.2 Relationship between radiation dose and Raman peak position*

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 260 As shown in Fig. 7A, the relationship between the accumulated radiation dose and the position of
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 261 the $\nu_3(\text{SiO}_4)$ Raman peak is complex. As the radiation dose increases, the $\nu_3(\text{SiO}_4)$ Raman peak of
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 262 zircon grains unaffected by annealing processes would be expected to broaden and shift towards
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 263 lower values (Fig. 1). However, the observed distribution fails to follow such a simple linear trend,
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 264 and zircon grains that have experienced a wide range of α -decay damage accumulation display the
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 265 same position of the Raman peak. Such an unexpected distribution is ascribed to different
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 266 temperature-time histories of source rocks.

267 Based on the fact that annealing of the zircon lattice proceeds step-by-step, as shown by laboratory
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 268 experiments (Murakami et al., 1991; Geisler, 2002), in our samples we identify three populations of
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 269 zircon grains following different trends in the α -dose vs. $\nu_3(\text{SiO}_4)$ -Raman-peak diagram (Fig. 7A).
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 270 The slopes of such trends can be quantitatively defined by means of a frequency plot where the
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 271 downshift of the Raman peak relative to 1008 cm^{-1} is related to the accumulated radiation dose (Fig.
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 272 7B).

273 *Trend 1* (Fig. 7), with the steepest negative slope matches well the expected pattern for unannealed
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 274 zircons (Fig. 1), whereas the other two trends indicate different temperature/time annealing paths.
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 275 *Trend 2* (Fig. 7), with intermediate slope, indicates only partial annealing, whereas *trend 3*, with the
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 276 gentlest slope, reflects a more extensive lattice recovery, which implies more recent annealing,
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 277 higher-temperature conditions, or longer thermal overprint.

278 Considering the overall similarity of slopes calculated for the three samples separately (from -3 to -
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 279 $8 \text{ cm}^{-1}/\alpha\text{-event mg}^{-1}$ for *trend 1*, from -0.9 to -1.7 for *trend 2*, and from -0.1 to -0.4 for *trend 3*), we
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 280 assumed that the source areas were affected by the same main thermal events. Data from all studied
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281 zircons thus allow us to more robustly define three lines – all sharing an intercept 1008 cm^{-1}
 282 (crystalline zircon) – with slopes -5.5 for *trend 1*, -1.5 for *trend 2*, and -0.4 for *trend 3* (Fig. 7C,
 283 7D, 7E). Each zircon grain was thus assigned to *trend 1*, 2, or 3 based on the trend line found
 284 within the shortest Euclidean distance. By this procedure, in each sample between 21% and 39% of
 285 zircon grains were assigned to *trend 1* (crystalline zircons), 27-49% of grains to *trend 2* (partially
 286 annealed zircons), and 20-44% of grains to *trend 3* (extensively annealed zircons).

288 6.3 Relationship between zircon age and metamict state

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 290 By combining U-Pb ages with the metamict state of each zircon grain, the age populations of zircon
 291 grains identified in the three samples can be split into diverse subpopulations. The relative
 292 proportions of such subpopulations vary from sample to sample.

293 Sample NH10 shows three age groups ($<0.7 \text{ Ga}$, 50%; $0.7\text{-}1.5 \text{ Ga}$, 48%; $>1.5 \text{ Ga}$, 2%). In the young
 294 group, 54% of zircon grains are crystalline (*trend 1*), 37% are partially annealed (*trend 2*), and 9%
 295 are extensively annealed (*trend 3*). In the intermediate age group, 25% of grains are crystalline,
 296 47% are partially annealed, and 28% extensively annealed. In the old group, all zircons appear to be
 297 extensively annealed.

298 Sample NH27 shows four age groups ($<0.3 \text{ Ga}$, 16%; $0.3\text{-}0.7$, 20%; $0.7\text{-}1.5 \text{ Ga}$, 53%; $>1.5 \text{ Ga}$,
 299 11%). In the youngest group, 90% of zircon grains are crystalline (*trend 1*), 10% are partially
 300 annealed (*trend 2*), and none is extensively annealed (*trend 3*). In the “Pan-African” age group, 23%
 301 of grains are crystalline, 31% are partially annealed, and 46% are extensively annealed. In the
 302 “Irumide” age group, 18% of grains are crystalline, 32% are partially annealed, and 50% are
 303 extensively annealed. In the oldest group, crystalline and partially annealed zircons represent 14%
 304 of the population each, and 72% are extensively annealed.

305 Sample NH45 has similar age populations with similar proportions of crystalline and metamict
 306 zircons as sample NH10 ($<0.7 \text{ Ga}$, 44%; $0.7\text{-}1.5 \text{ Ga}$, 51%; $>1.5 \text{ Ga}$, 5%). In the young group, 41%

of zircon grains are crystalline (*trend 1*), 33% are partially annealed (*trend 2*), and 26% are extensively annealed (*trend 3*). In the intermediate age group, only 10% of grains are crystalline, 61% are partially annealed, and 29% are extensively annealed. In the old group, crystalline zircons are lacking, 67% of grains are partially annealed, and 33% are extensively annealed. Data indicate an increase of extensively annealed zircons in the oldest populations, whereas young zircons (Panafrican in age, or younger) were less affected by thermal annealing.

6.4. Identification of the annealing events

Each zircon grain plotting to the right of the expected trend between Raman peak position and accumulated α -damage indicates thermal annealing (Figs. 1 and 7A). If the age of major thermal events associated with either igneous activity or orogenic metamorphism in potential source rocks is known, then these ages can be used to calculate the α -doses (equation 1) accumulated after those thermal events that may have restored the zircon crystalline structure damaged by α -decay since crystallisation. If the thermal history of source areas is poorly constrained, or in ancient settings where source terranes have been entirely eroded, then the age of the main thermal events can be inferred to correspond to the main age peaks obtained by U-Pb dating.

The newly calculated α -doses based on the estimated age of the thermal event are lower than those for the original crystallization, and reflect the damage accumulated after the annealing event (Nasdala et al., 2001). By iteratively calculating the α -doses accumulated since each potential thermal event, each zircon grain is thus progressively shifted to the left in an α -dose vs. $\nu_3(\text{SiO}_4)$ -Raman-peak position diagram for younger and younger thermal events, until the expected trend is reached (Fig. 8). In this way, we can assess for each grain which is the most likely age of the last major thermal-annealing event. Such an age would be generally older than the stratigraphic age of the sample. Annealing occurring after deposition within the sedimentary basin rather than in the

332 source area is inferred when all zircons display annealing ages that are younger than the age of the
 1
 333 sediment. Alternatively, individual zircon grains that plot along *trends 2* or *3* even when
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 334 accumulated damage has been calculated using the age of the youngest annealing event might be
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 335 expected if the analysed grains underwent multiple annealing events. In this latter case, each event
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 336 contributed to restore the crystallinity in spite of the continuous increase of α -doses since original
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 337 crystallization. This effect will cause the $\nu_3(\text{SiO}_4)$ -Raman-peak position to be notably higher than
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 338 expected from the accumulated doses, thus leading to postulate very young annealing ages that may
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 339 not correspond with actual thermal events. This is because the α -dose would need to be reduced
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 340 considerably (i.e. calculated using a very young age in equation 1) to restore a normal $\nu_3(\text{SiO}_4)$ -
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 341 Raman-peak position/accumulated dose ratios (i.e. along *trend 1*).

24
 342 In our African case study, the main thermal events to be considered took place around ~ 1.0 Ga
 26
 343 (Irumide orogeny; [De Waele et al., 2009](#)), ~ 0.6 Ga (Pan-African orogeny; [Fritz et al., 2013](#)), 280-
 28
 29
 344 180 Ga (Permian to Early Jurassic Karoo igneous events; [Jourdan et al., 2006](#); [Daszinnies et al.,](#)
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 345 [2009](#)), and ~ 120 Ma (Mozambique basin magmatism; [König and Jokat, 2010](#)). Therefore, for each
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 346 zircon grain plotting outside of the expected trend between Raman peak position and accumulated
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 36
 347 α -damage (i.e. *trends 2* and *3* in [Fig. 7C, 7D, 7E](#)) we calculated a new α -dose according to *equation*
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 348 *1*, using 1.0, 0.6, 0.26, and 0.12 Ga. as approximate ages of these thermal events. Uncertainties in
 40
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 349 Raman data, U-Th concentrations, and age of the thermal events were considered by calculating an
 43
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 350 α -dose corresponding to the given age of the thermal event $\pm 10\%$. The age of the last thermal event
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 351 can be inferred as the age corresponding to the α -dose for which each zircon plots closest to *trend 1*
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 352 ([Fig. 8](#)).

354 6.5. Assessing the effect of annealing events

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356 Annealing of metamict zircons affects the relationship between Raman peak position and radiation
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357 dose, because the $\nu_3(\text{SiO}_4)$ -Raman-peak position is shifted toward the crystalline value of 1008 cm^{-1}
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358 independently of the radiation dose accumulated since crystallization (Fig. 7B). Unannealed zircon
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359 grains display highest $\Delta\text{peak}/\text{dose}$ values, where Δpeak indicates the difference between a $\nu_3(\text{SiO}_4)$ -
8
360 Raman-peak position of 1008 cm^{-1} (crystalline zircon) and the actual peak position. Annealed
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361 zircons have higher crystallinity than expected from their age and actinide content. They should
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362 thus display a lower $\Delta\text{peak}/\text{dose}$ ratio, which is closer to that of unannealed grains for older thermal
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363 events (because they have been accumulating damage for a longer time since annealing) and
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364 becomes progressively lower for younger thermal events. By means of a U-Pb age vs. $\Delta\text{peak}/\text{dose}$
21
365 plot we can thus evaluate the impact of the thermal events identified for each annealed zircon grain
23
366 (following the approach described in section 6.4) on the different age populations of detrital zircons
26
367 (Fig. 9). For the same annealing event, older zircon grains show lower $\Delta\text{peak}/\text{dose}$ ratios, because
28
368 of the higher doses accumulated since crystallization leading to incomplete annealing. Twenty-five
31
369 grains (9% of the entire dataset), mostly displaying extensive annealing (*trend 3*), plot very low
33
370 along the $\Delta\text{peak}/\text{dose}$ axis, indicating “extreme” crystallinity with respect to the accumulated dose.
36
371 For these grains, the youngest thermal event (Cretaceous in age) was found to be insufficient to
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372 restore their peak position vs. dose relationship to normal values (*trend 1*). As the depositional age
39
40 of sample NH10 post-dates the Early Cretaceous volcanic activity in the Mozambique channel, the
41
42 occurrence of younger thermal events is ruled out, as well as annealing during burial after
44
45 deposition, because all zircons would be affected by such event. The easiest explanation for such
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47 extremely high $\Delta\text{peak}/\text{dose}$ ratios is that these grains were involved in multiple annealing events,
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49 each of them contributing to increase their crystallinity.
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381 crystallization age of 118 Ma and a post-Cretaceous annealing age. Because the young
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 382 crystallization age of this zircon rules out the effect of multiple annealing events, it should be either
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 383 older or less crystalline to fit in our scheme. Its anomalous $\nu_3(\text{SiO}_4)$ -Raman-peak position vs. α -
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 384 dose relationship thus suggests that Raman and U/Pb spots have targeted different domains within
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 385 the same zircon grain.

387 **7. Improving provenance discriminations**

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 389 U-Pb age spectra of detrital zircons contained in the three studied samples allow discrimination of
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 390 four main primary provenances: Archean-Paleoproterozoic terranes, the Irumide orogen, the Pan-
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 391 African orogen, and Lower Cretaceous volcanic rocks. Considering that zircon-bearing magmatic or
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 392 metamorphic rocks of ~ 1 Ga or ~ 0.6 Ga occur throughout the Irumide and Pan-African belts widely
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 393 exposed across southern Africa from Namibia to Mozambique and from Zimbabwe to Zambia, and
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 394 that zircon grains can be recycled from siliciclastic sedimentary rocks an unknown number of times,
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 395 such a provenance estimation is too vague to help us to pin-point actual sediment sources
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 396 univocally. A more accurate identification of the potential sources and dispersal paths of zircon
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 397 grains can be achieved by combining U-Pb dating with Raman spectroscopy, allowing us to
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 41
 398 distinguish four to five different subpopulations of similarly aged grains with different thermal
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 399 histories (Fig. 10).

400 In the Valanginian/Hauterivian sample NH45, partially annealed *trend 2* zircons mostly represent
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 48
 401 Irumide ages that were affected by both Pan-African and Karoo thermal events, whereas those
 50
 402 yielding Pan-African ages recorded Late Permian and Early Jurassic events. Source areas most
 52
 53
 403 likely located south of Lake Malawi are suggested for most of these partially annealed grains based
 54
 55
 404 on the present distribution of rocks matching such a complex geological evolution (Fig. 2). Most
 57
 58
 405 Irumide and Pan-African *trend 3* zircons record a complex, possibly multi-phased annealing history
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 60
 406 (Fig. 10), as the youngest known annealing event (Early Cretaceous) is insufficient to restore a

407 normal dose/peak ratio. The occurrence of unannealed zircons (*trend 1*) limits the chances of post-
 1
 408 depositional annealing during burial.

409 A drastic provenance change is documented by the Aptian/Albian sample NH27, where many
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 410 zircons yielded Early Cretaceous ages and were thus generated from penecontemporaneous
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 411 volcanism in coastal Mozambique. These zircons show no sign of subsequent annealing. Partially
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 11
 412 annealed *trend 2* zircons of both Irumide and Pan-African-ages were largely affected by the Late
 12
 13
 413 Permian event. Among *trend 3* zircons, a few grains with the oldest U-Pb ages were finally
 14
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 16
 414 annealed in the Late Permian, several Irumide-aged zircons in the Early Jurassic and Early
 17
 18
 415 Cretaceous, and Pan-African-aged zircons show a complex history.

416 In the Cenomanian/Turonian sample NH10, zircon populations are remarkably similar as those in
 19
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 417 sample NH45, with a more extensive Pan-African effect on partially annealed *trend 2* Irumide-aged
 22
 23
 418 zircons. The Early Cretaceous thermal event, lacking in the oldest sample NH45, is recorded by
 24
 25
 419 ~10% of the analysed zircons in sample NH10. *Trend 3* zircons of Pan-African age were affected
 26
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 420 by the Early Cretaceous thermal event, or were involved in multiple annealing stages, whereas
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 421 Irumide-aged *trend 3* zircons also display annealing during Permian and Jurassic.
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422 8. Conclusions

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 425 The innovative combination of Raman spectroscopy with classic LA-ICP-MS U-Pb dating on the
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 426 same zircon grains leads to a sharp improvement of resolution power in provenance analysis of
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 47
 427 detrital zircon. The $\nu_3(\text{SiO}_4)$ Raman peak of zircon crystals broadens and shifts to a lower position
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 428 with increasing metamict state. These features allow us not only to discriminate among zircon
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 429 grains with different metamict state and different degrees of annealing but also to estimate a
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 430 geologically viable age for the annealing event. Identifying different zircon subpopulations with the
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 431 same crystallization age but different subsequent thermal histories adds further cogent constraints
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 432 that allow us to discriminate among different potential source terranes with similar ages of crustal
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433 growth and thus to pinpoint detrital sources considerably reducing ambiguities and improving
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434 provenance diagnoses.

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436 ACKNOWLEDGMENTS

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437
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597 FIGURE CAPTIONS

598

599 **Figure 1.** Progressive degree of metamictization as revealed by Raman spectroscopy in zircon
600 crystals with complete accumulation of radiation damage. **Upper panel)** Increasing full width at
601 half maximum (FWHM) of the $\nu_3(\text{SiO}_4)$ Raman peak with damage accumulation (data after [Nasdala](#)
602 [et al., 2001](#)). **Lower panel)** Shifting position of the $\nu_3(\text{SiO}_4)$ Raman peak with damage
603 accumulation (FWHM data after [Nasdala et al., 2001](#), converted using *equation 2*).

604

605 **Figure 2.** Sketch geological and geochronological map of Mozambique, Malawi, and Zambia (after
606 [Hanson, 2003](#), [DeWaele et al., 2006](#), [Jourdan et al., 2006](#) and [Goscombe et al., 2019](#)). Different
607 terranes with age of crustal growth ranging widely from Archean to Cambrian were affected by
608 diverse younger stages of thermal overprint, the most intense of which took place during the
609 Neoproterozoic Pan-African orogeny.

610

611 **Figure 3.** Deconvolution of Raman peaks in one zircon grain from sample NH10. Peak position and
612 full width at half maximum (FWHM) are indicated.

613

614 **Figure 4.** U-Pb age-spectra of detrital zircons in samples NH45, NH27 and NH10 (age vs.
615 frequencies plotted as Kernel Density Estimates using the *provenance* package of [Vermeesch et al.,](#)
616 [2016](#)).

617

618 **Figure 5.** Inverse correlation between position and full width at half maximum of the $\nu_3(\text{SiO}_4)$
619 Raman peak (R^2 0.80). A narrow peak at $\sim 1008 \text{ cm}^{-1}$ is diagnostic of fully crystalline grains,
620 whereas lower positions and wider peaks indicate a progressive degree of metamictization ([Nasdala](#)
621 [et al., 1998](#)).

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623 **Figure 6.** Relationships of zircon U-Pb ages with accumulated α -dose and $\nu_3(\text{SiO}_4)$ Raman peak.
 1
 624 The lack of strongly metamict old zircon grains suggests lower chemical and/or mechanical
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 625 durability and hence selective loss during repeated sedimentary cycles.
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 627 **Figure 7.** Identifying different thermal histories of detrital zircons. **A)** Complex relationship
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 628 between accumulated radiation dose and $\nu_3(\text{SiO}_4)$ Raman peak position. The grey area represents
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 629 the field of nearly complete accumulation of damage calculated from zircons reported in [Nasdala et](#)
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 630 [al. \(2001\)](#). **B)** Definition of the three annealing trends by plotting the downshift of the Raman peak
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 631 relative to 1008 cm^{-1} *versus* radiation dose for each zircon grain. **C, D, E)** Partitioning among
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 632 *trends 1, 2 and 3* of zircon grains in samples NH10, NH27, and NH45.
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 634 **Figure 8.** Identification of the annealing event. For each zircon, the $\nu_3(\text{SiO}_4)$ Raman peak
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 635 position/accumulated α -dose should lie on *trend 1* (white square). If the calculated α -dose (grey
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 636 square) is greater than that expected following *trend 1* (complete accumulation of damage) for the
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 637 measured position of the $\nu_3(\text{SiO}_4)$ Raman peak, the zircon grain was thermally annealed.
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 638 We can estimate the age for which the accumulated α -damage would match the crystallinity of the
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 639 zircon with a trial and error approach. By using the ages of potential annealing events known for
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 640 inferred source areas, we recalculate the accumulated α -damage from the age of each thermal event
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 641 (coloured circles). Accumulated α -doses will be lower and lower for younger and younger thermal
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 642 events, until *trend 1* is eventually reached. The oldest event, whose age restores the normal $\nu_3(\text{SiO}_4)$
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 643 Raman peak position *vs* radiation dose ratio (*trend 1*), is taken as the age of annealing.
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 645 **Figure 9.** Discriminating subpopulations of detrital zircons with same crystallization age
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 646 (determined by U-Pb geochronology) but different annealing history (determined by Raman
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 647 spectroscopy). Nearly one third of the analysed zircon grains show no thermal annealing. The

648 Karoo event is estimated to have affected > 25% of analysed grains, resulting to be a major thermal
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649 event, whereas fewer grains recorded Jurassic, Early Cretaceous or Pan-African heating. About 7%
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650 of zircon grains yielded low $\Delta_{\text{peak}}/\text{dose}$ ratio, indicating very recent annealing or, more probably,
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651 multiple annealing events through time. Note that all zircons older than 1.3 Ga underwent thermal
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652 annealing. The zircon grain from sample NH27 denoted with the symbol * is anomalous: it should
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653 either have a greater $\Delta_{\text{peak}}/\text{dose}$ ratio (unannealed zircon) or should yield an older age.
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655 **Figure 10.** Provenance discrimination of detrital zircons improved. Several subpopulations of
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656 zircon grains with similar age but different thermal histories can be distinguished by combining U-
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657 Pb dating and analysis of the position of the $\nu_3(\text{SiO}_4)$ Raman peak. For each sample, the relative
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658 proportions of grain-age populations based on U-Pb age (thick bar), crystallinity (intermediate bar),
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659 and age of annealing events (thin bar) are given. Note that the combined-age fingerprints of samples
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660 NH45 and NH10 are similar, and distinct from those of sample NH27. When the age of the
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661 annealing event is taken into account, the Karoo thermal event affected most zircons in sample
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662 NH45, whereas Cretaceous heating characterizes annealed zircons in sample NH10.
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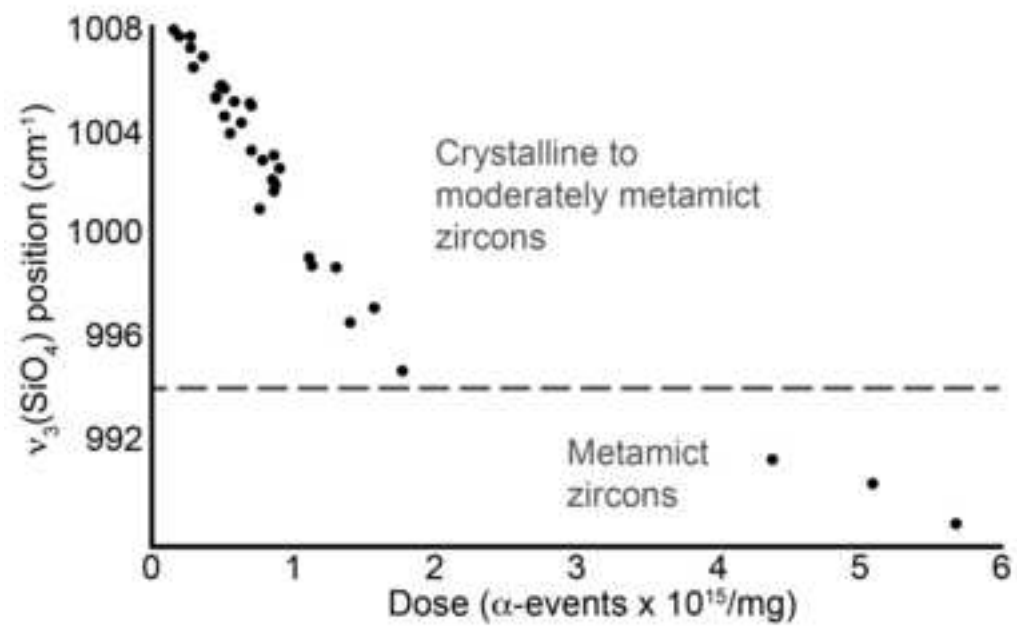
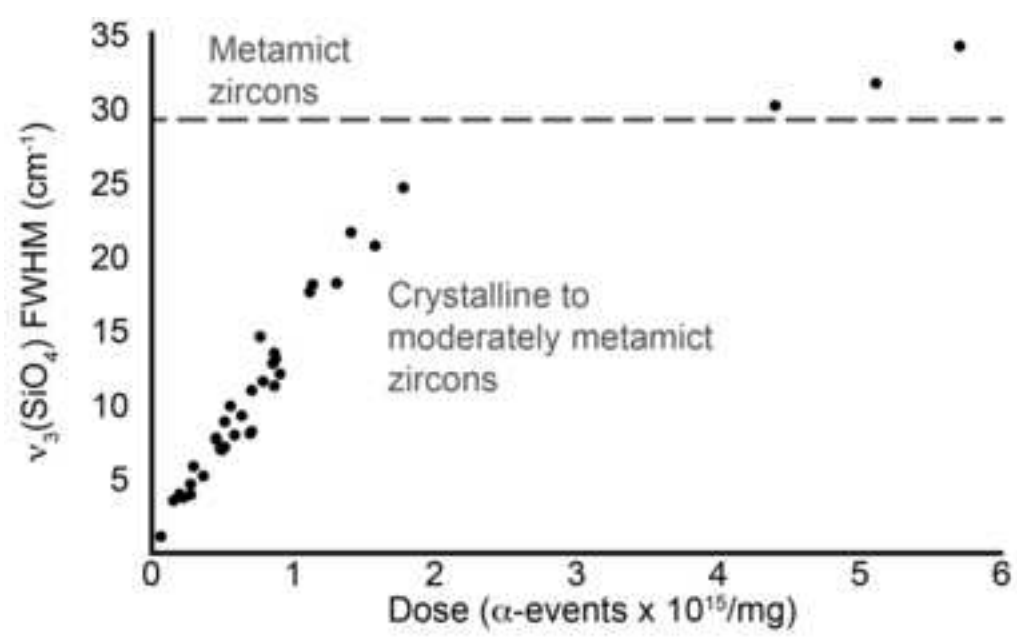


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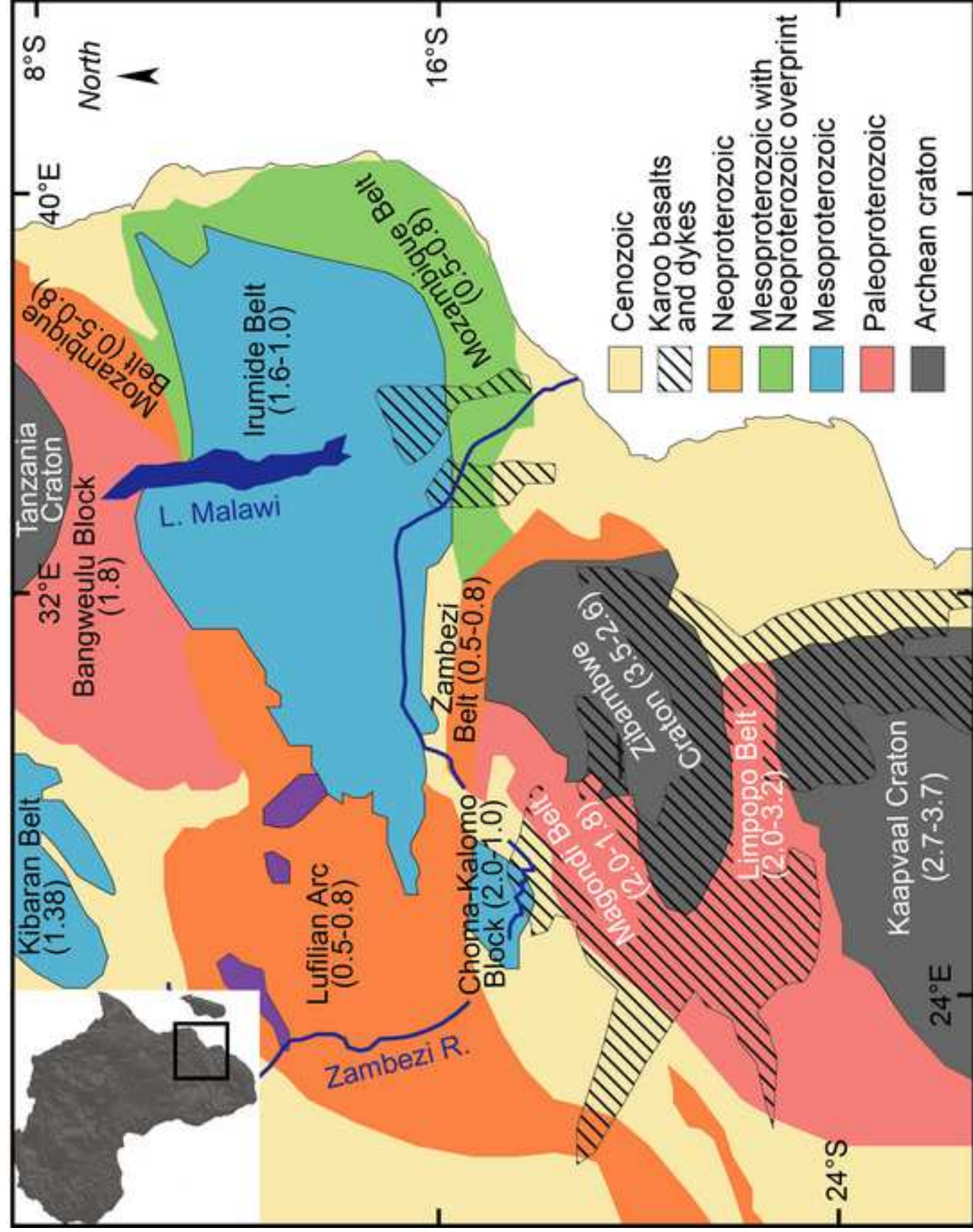


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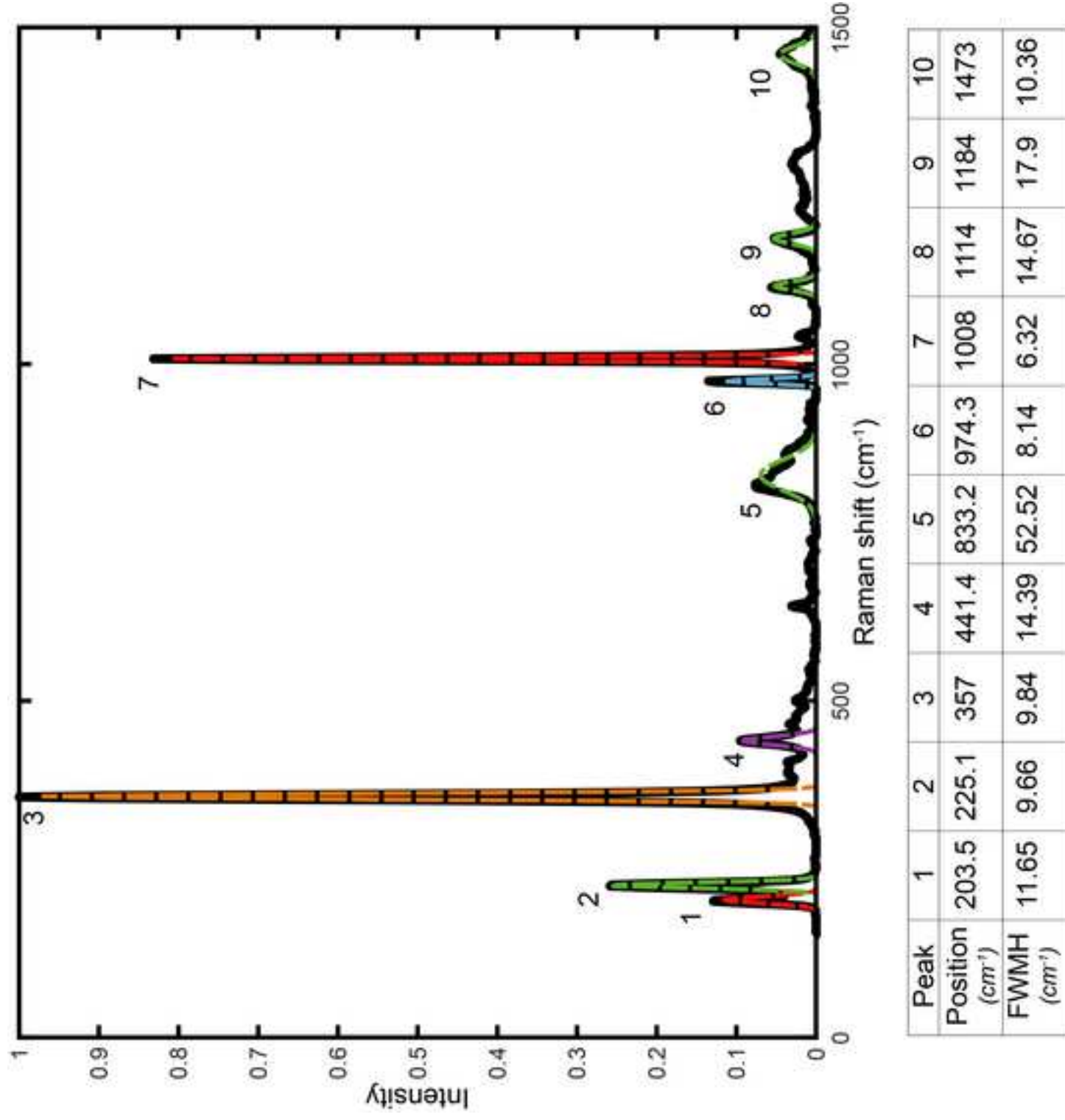


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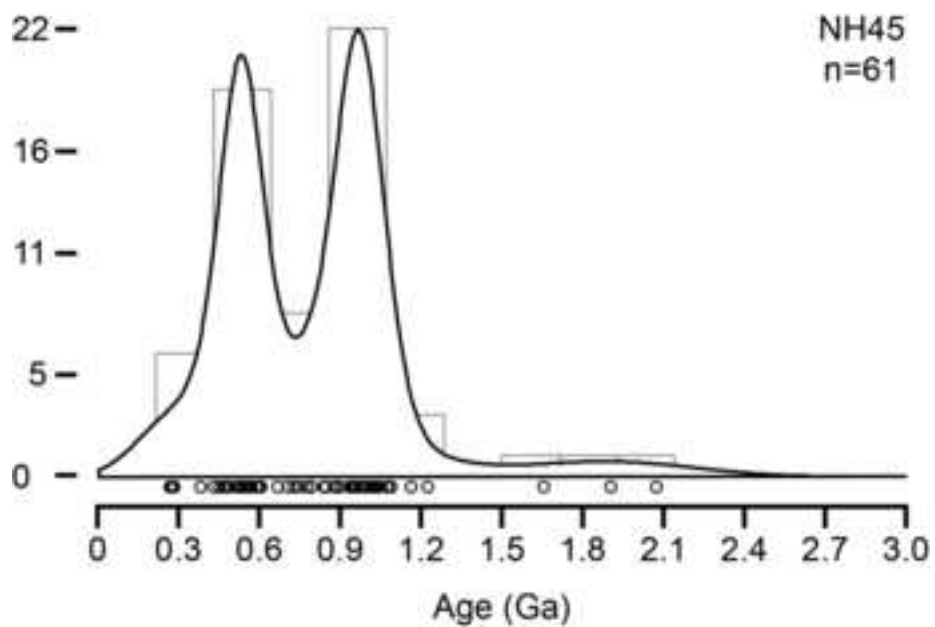
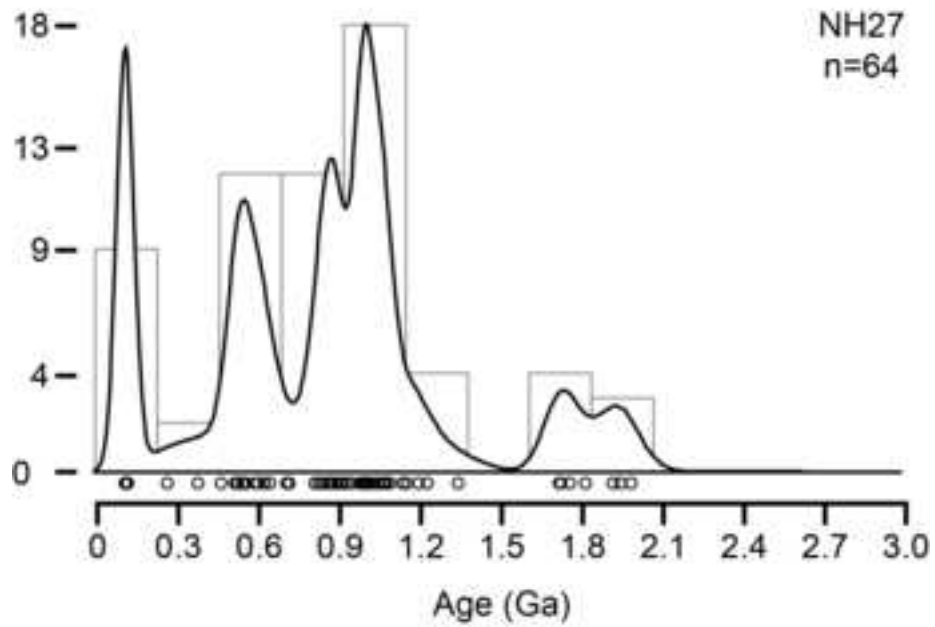
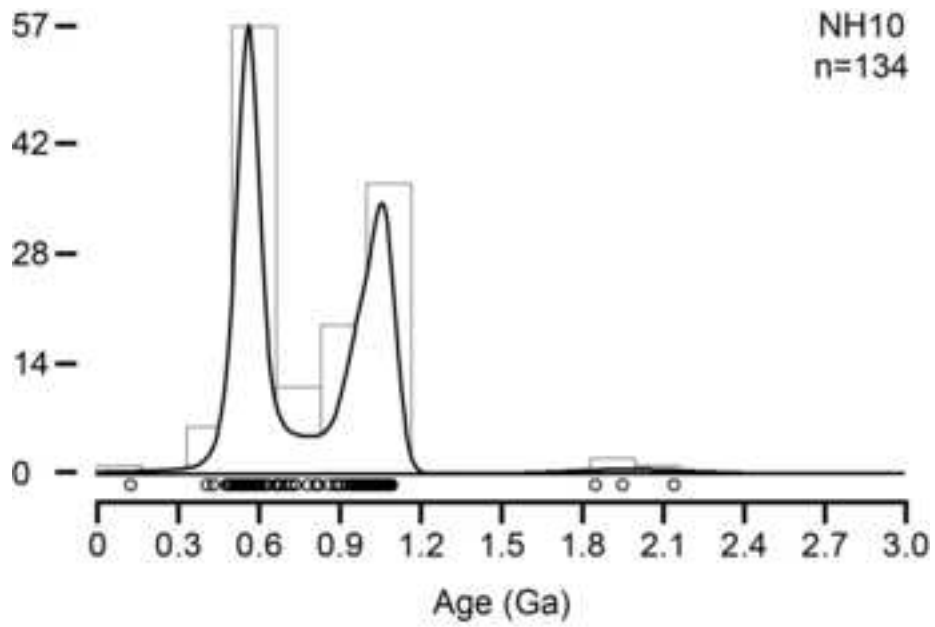


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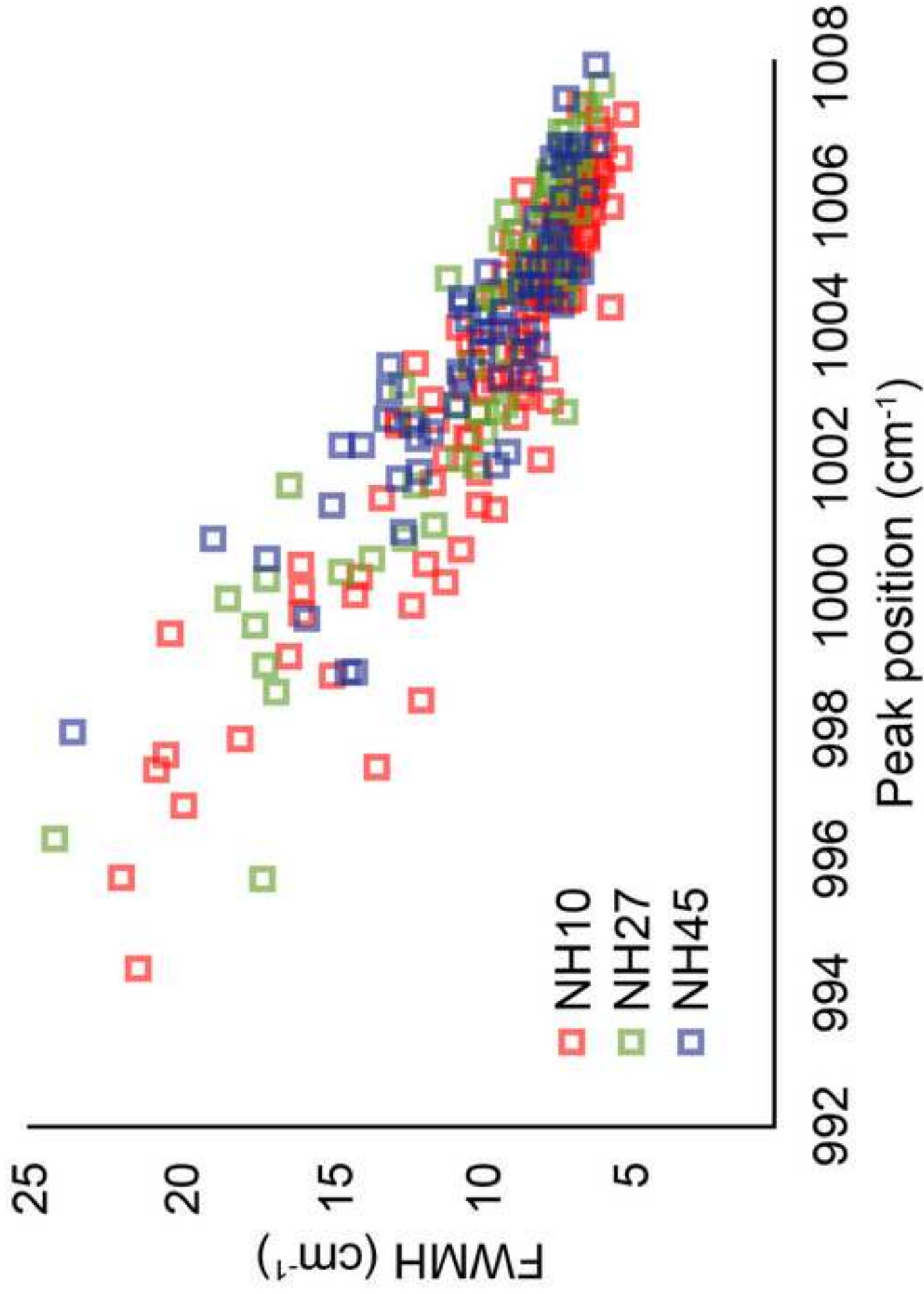


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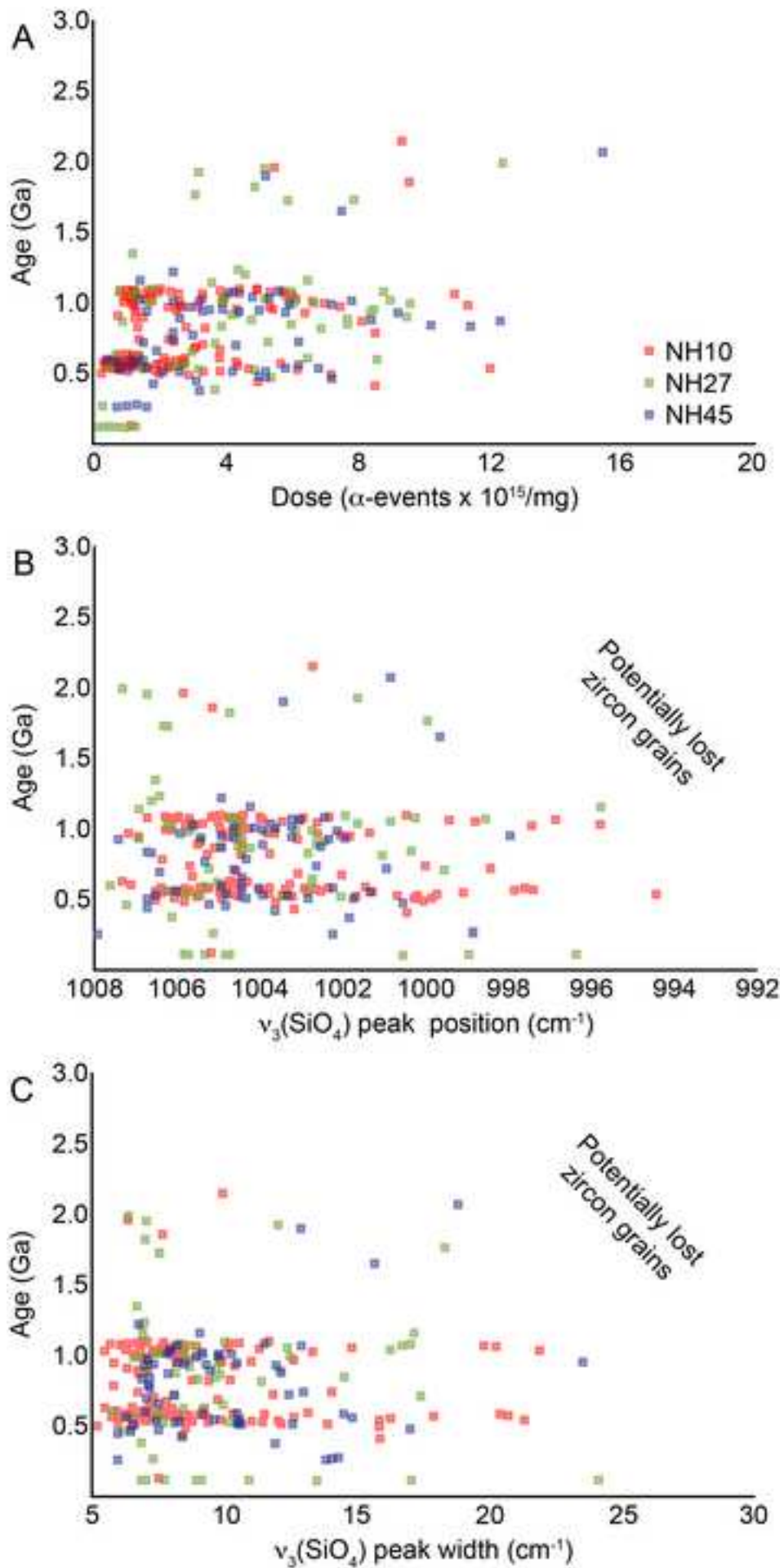


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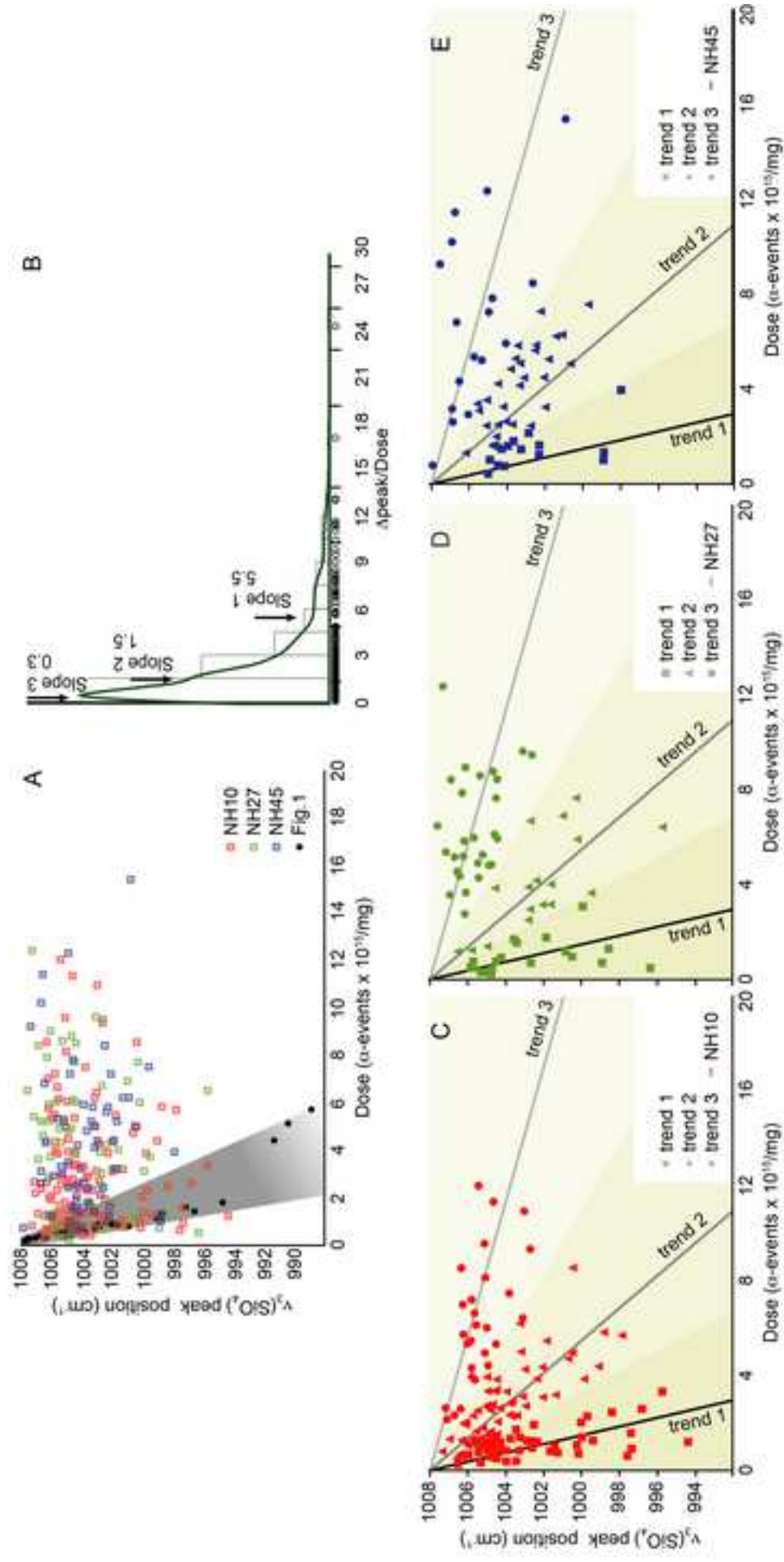


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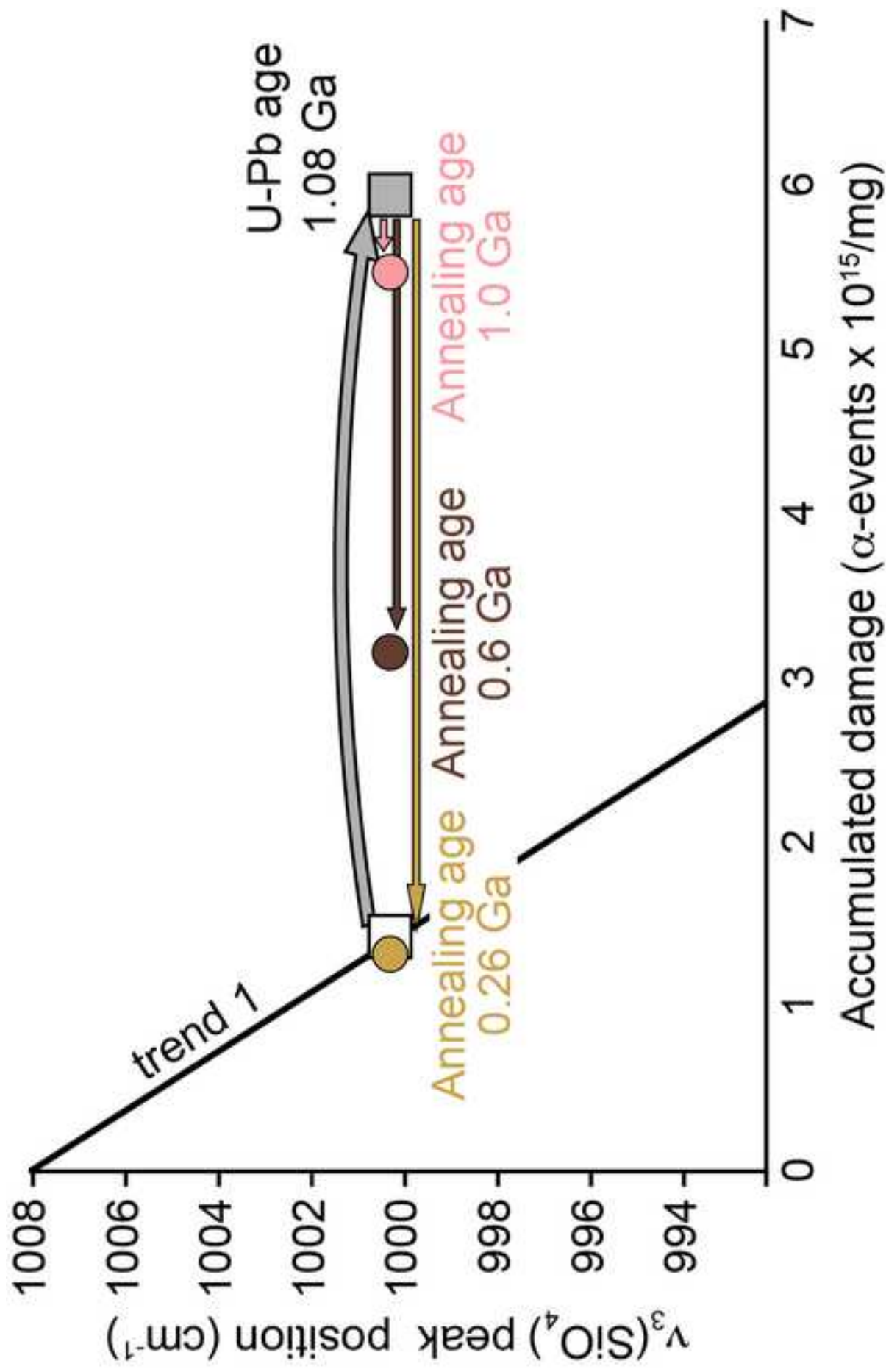


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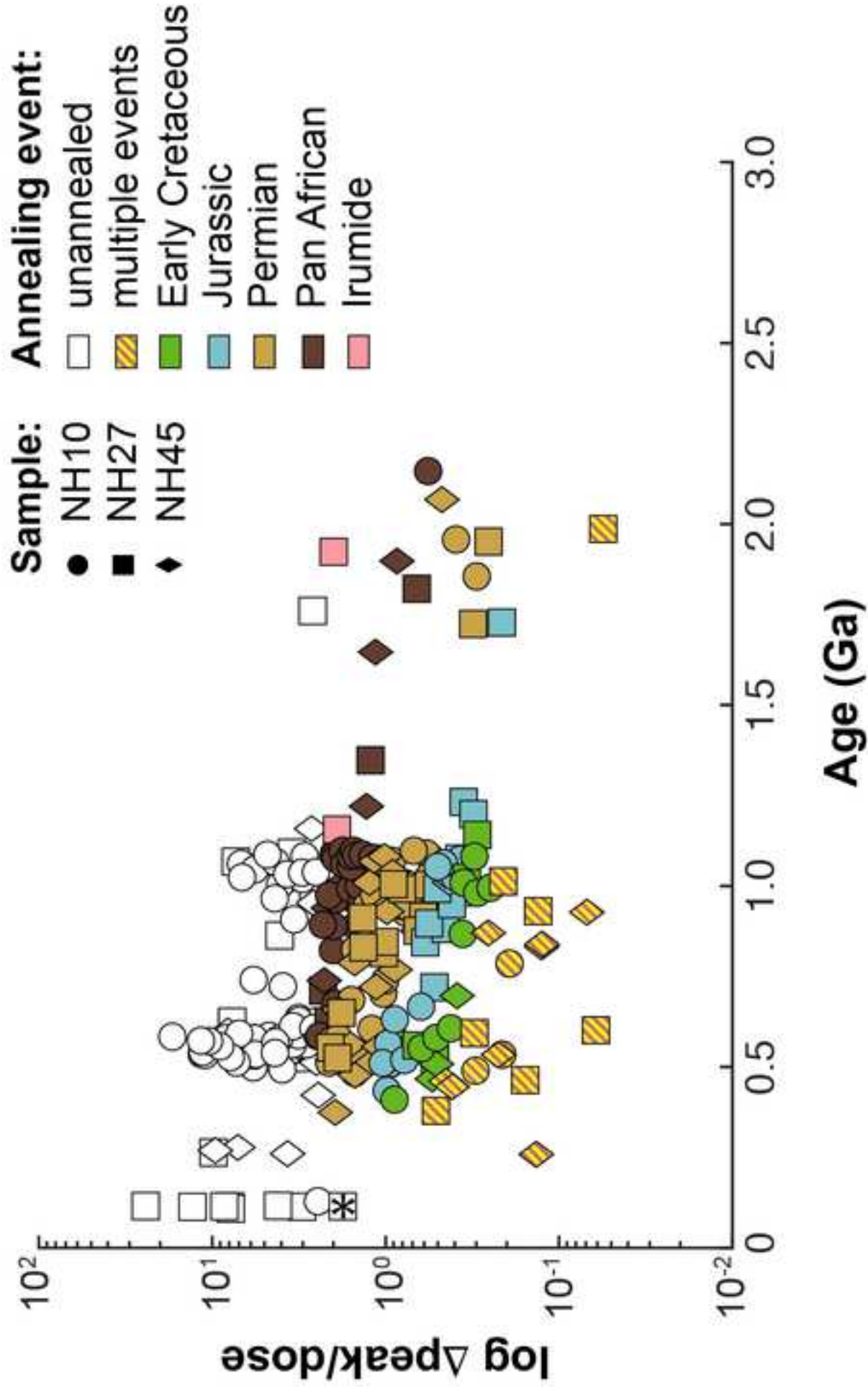


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