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Petrogenetic processes at the tipping point of plate tectonics: Hf-O isotope ternary modelling of Earth's last TTG to sanukitoid transition

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Highlights

Zircon Hf-O evidence supports recycled oceanic crust and continental crust growth during the magmatic lull;

Deep mantle penetration of subduction material marks a sporadic episode of sanukitoid magmatism;

Youngest TTG-sanukitoid transition is the last vestige of an ante-plate tectonics regime;

Global TTG-sanukitoid magmatic transition is a protracted, diachronous process and spans at least 800 Myr.

Abstract

Modern style plate tectonics is characterized by one-sided subduction and continental margin basalt-andesite-dacite-rhyolite (BADR) magmatism, whereas continental magmatic rocks in the Archaean record had tonalite-trondjemite-granodiorite (TTG) composition. Their main difference is the absence (in the modern style) and the presence (in the ancient style) of abundant juvenile, basalt-derived felsic magmatism. The diversity of modern continental magmas depends partly on metasomatic processes in the mantle wedge providing sediment input (melt/fluid). Contrasting scenarios in the rock record therefore are the presence or absence of (1) basalt-derived melt (TTG) and (2) sedimentary input to the magmas. A late, "Archaean-style" tectonic regime is recorded in the Palaeoproterozoic Mineiro Belt (Brazil) using whole-rock geochemistry of its plutons coupled to zircon Hf and O isotopes from these rocks and from detrital grains from the local (meta)sediments. Increasing $\delta^{18}\text{O}$ with decreasing $\varepsilon_{\text{Hf}(t)}$ values in zircon indicate oceanic crust recycling and input of sediments to the mantle wedge during the Palaeoproterozoic. Since some form of early subduction including the formation of a mantle wedge has occurred since the Mesoarchaeon, it seems that the onset of subduction and the final establishment of modern plate tectonics at the global scale are temporally distinct. The latter did not occur until the Palaeoproterozoic. Prior to this time ("ante-plate tectonics"), punctuated subcretion/subduction marks a gestational stage that took c. 800 Myr to transition diachronously to a truly global mechanism. The TTG-sanukitoid transition, which signals the opening of a mantle wedge, occurred in the Mineiro Belt during the early Proterozoic "magmatic lull" and thus represents the last gasp of the ante-plate tectonics regime.

42 **Keywords:** Subduction, Plate tectonics, TTG-sanukitoid transition, Hf-O zircon modelling

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47 *The authors have no competing interests to declare.*

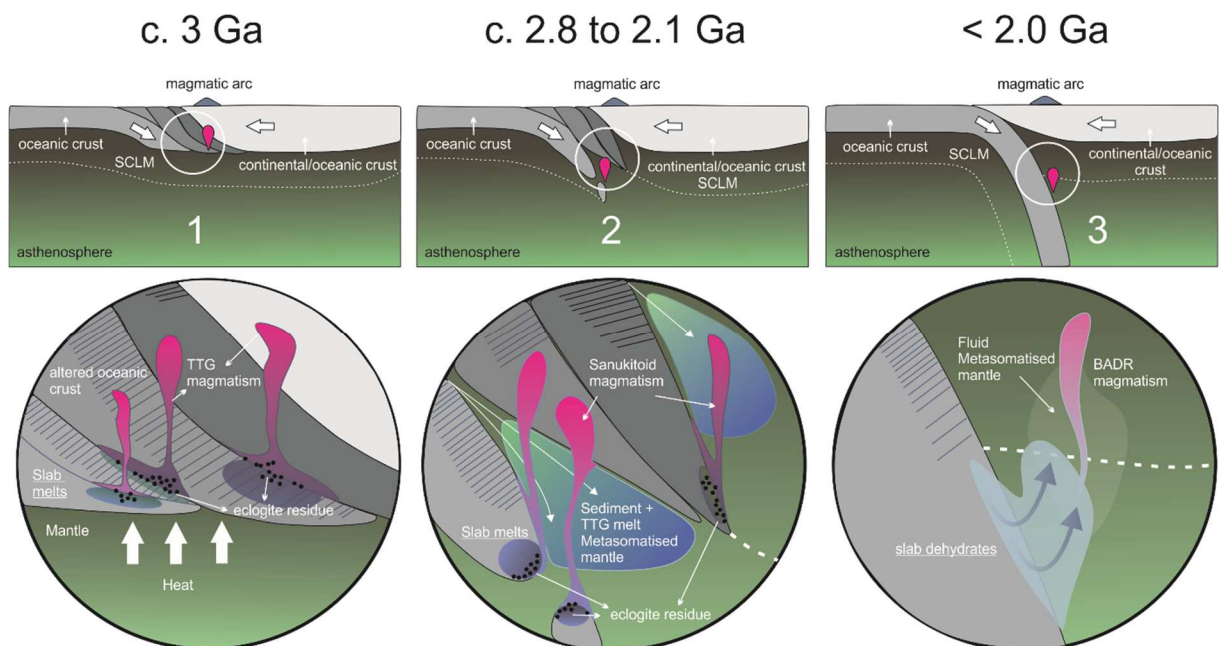
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49 **1 - Introduction**

50 The composition of the early continental crust and the evolution of plate
51 tectonics are subjects of current debate, with ideas varying from a stagnant mafic lid to a
52 felsic and dynamic proto-crust (e.g. [Bédard, 2018](#); [Nebel et al., 2018](#); [Cawood et al.,](#)
53 [2018](#)). However, the onset of mobile lid plate tectonics is widely inferred to have started
54 at c. 3.0 Ga when early vertical tectonics progressed to a horizontal style ([Beall et al.,](#)
55 [2018](#) and references therein), although mobile lid behaviour in the evolution of
56 Eoarchean terranes has been inferred in Greenland and Canada (e.g. [Cawood et al., 2018](#);
57 [Nebel et al., 2018](#)). By 3.0 Ga, several other lines of evidence suggest mobility of tectonic
58 plates, marked by shallow subduction and increased reworking of previously-existing
59 crust (e.g. [Dhuime, et al., 2018](#); [Cawood et al., 2018](#)). During this period, magmatism was
60 dominated by tonalite-trondjemite-granodiorite suite rocks (TTGs), formed by partial
61 melting of alkali-rich basalt sources (e.g. [Moyen and Martin, 2012](#) and references
62 therein; [Moyen and Laurent, 2018](#)) and/or melting of oceanic plateau basalts ([Hastie et](#)
63 [al., 2016](#)). Sanukitoid magmas are petrogenetically more complicated successors to
64 TTGs, being derived from mixed crustal and mantle reservoirs as indicated by high LILEs
65 often with 'enriched' radiogenic isotopes and high $\delta^{18}\text{O}$, combined with high Mg# and
66 transition metals (e.g. [Shirey and Hanson, 1984](#); [Martin et al., 2009](#)). These
67 characteristics have been explained by steepening of the subducted oceanic slab and
68 consequent opening of a mantle wedge, which could then interact with slab-derived (i.e.
69 crustal) fluids and melts ([Moyen and Martin, 2012](#)), including TTG magmas and/or
70 subducted sediments. Therefore, the transition from TTG to sanukitoid magmas is often

71 inferred to mark the onset of subduction-driven plate tectonics caused by Earth's
 72 cooling, which then evolves to modern-style subduction-related magmatism (basalt-
 73 andesite-dacite-rhyolite - BADR, Fig. 1). Alternatively, this transition could have been
 74 caused by subcretion of plates or pseudo-subduction (Bédard, 2018), not characterising
 75 a regime of modern-style plate tectonics, but still providing evidence for plate mobility
 76 (Fig. 1).

77



78

79 **Figure 1:** Diagrams with three tectonics scenarios for the Earth. Left: simplified geodynamics of an
 80 Archaean convergent setting characterized by stacking of oceanic slab and the lack of generation of mantle
 81 wedge and deep subduction. The subduction is mostly flat and the plate melts before it gets deep;
 82 produces TTG-like magmas and eclogite as residue. Centre: Sanukitoid magmas are formed in a 'thrust
 83 belt subcretion' scenario. The TTG magmas interact with a mantle wedge metasomatised by sediments
 84 and/or previous interaction with older TTG melts. Right: simplified geodynamics of a Phanerozoic
 85 convergent setting with deep subduction and dehydration of the plate. In all three scenarios, there are
 86 lateral and vertical movement of the edge of plates (i.e. plate tectonics is active), but because of different
 87 geothermal conditions and rheology of the different scenarios, the panel on the left and central case are
 88 not considered subduction in this study, but subcretion.

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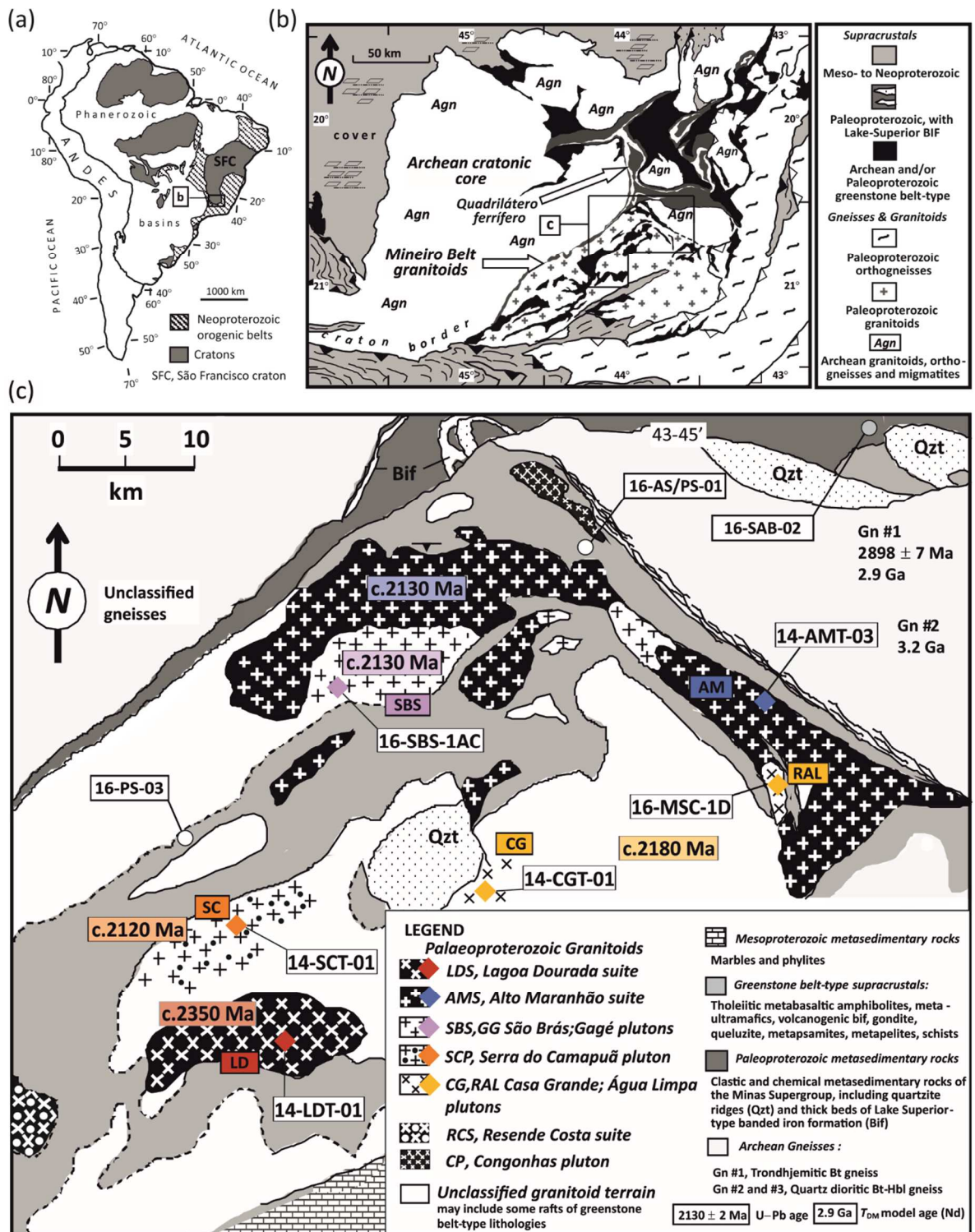
90 There is a trend in the current literature to establish a modern plate tectonic
 91 regime at the boundary between the Archaean and Palaeoproterozoic, meaning 2.5 Ga
 92 (e.g. Cawood et al., 2018 and references therein), but two points have yet to be fully
 93 understood: firstly, the TTG-sanukitoid transition was diachronous over nearly 1 Ga

94 because the last documented transition occurred from 2.35 to 2.1 Ga ([Moreira et al.,](#)
95 [2018](#)); therefore the same tectonic scenarios must have coexisted on Earth from c. 3 to 2
96 Ga, even if in different proportions. The second point is that if TTGs and sanukitoids
97 were not formed by what is considered modern subduction tectonics (e.g. [Stern, 2018](#)),
98 it should be argued that the latter did not operate before 2.1 Ga, as opposed to what is
99 converging as an agreement in the literature (e.g. [Nebel et al., 2018](#); [Cawood et al.,](#)
100 [2018](#)).

101 In this study, we contribute to the current debates surrounding the secular
102 evolution of granitoids and whether horizontal tectonics require modern-style
103 subduction. For this, we present oxygen, U-Pb and Lu-Hf isotope data in zircons from
104 igneous and sedimentary rocks of the early Proterozoic Mineiro Belt, Brazil. The three
105 isotope systems combined have long proved to be a powerful tool in understanding
106 tectonic settings, magma generation, recycling and crustal growth (e.g. [Hawkesworth](#)
107 [and Kemp 2006](#); [Hopkinson et al., 2017](#)). The Mineiro Belt rocks contain the youngest
108 TTG-sanukitoid geochemical transition yet reported (c. 2.1 Ga), and thus represent the
109 final vestige of the earlier regime, after which plate tectonics was truly global. They also
110 occupy the proposed (but narrowing) global magmatic lull and therefore contribute to
111 knowledge of a period when little 'juvenile' magmatism is known ([Spencer et al., 2018](#)).
112 The data are used to place constraints on TTG and sanukitoid petrogenesis at 2.1 Ga and
113 are further compared to well-established Archaean TTG-sanukitoid provinces.
114 Ultimately, the data have implications for both the proposed subcretion regime in plate
115 tectonics and the contribution of early mantle-derived sources in younger juvenile
116 terranes. Overall, we advocate non-modern subduction (ante-plate tectonics) on Earth
117 prior to 2.1 Ga, when the first low dT/dP rocks also appeared and modern calc-alkaline
118 magmas began to dominate the geological record ([Brown and Johnson, 2018](#)).

119 **2 – Geological context**

120 The São Francisco Craton (SFC) comprises a mosaic of various Archaean blocks
121 composed of TTGs and greenstone belts sutured in the Palaeoproterozoic at around 2.1
122 Ga and shielded from magmatism and significant deformation/metamorphism from a
123 later Neoproterozoic orogeny (e.g. [Heilbron et al., 2017](#) and references therein) ([Fig. 2a](#)).
124 The Palaeoproterozoic occurrences are broadly discriminated either as Archaean
125 reworked palaeocrust or juvenile arcs/plateaus. The current margins of the craton mark
126 its last deformation during the Neoproterozoic ([Heilbron et al., 2017](#)) ([Fig. 2b](#)). The area
127 of interest in this study encompasses the southern portion of the SFC, where the
128 Archaean basement is bounded to the south by a geologically distinct terrane, known as
129 the Mineiro Belt ([Fig. 2c](#)). The terminology palaeocraton, which follows, denotes any of
130 the Archaean portions of the craton amalgamated in the Palaeoproterozoic.

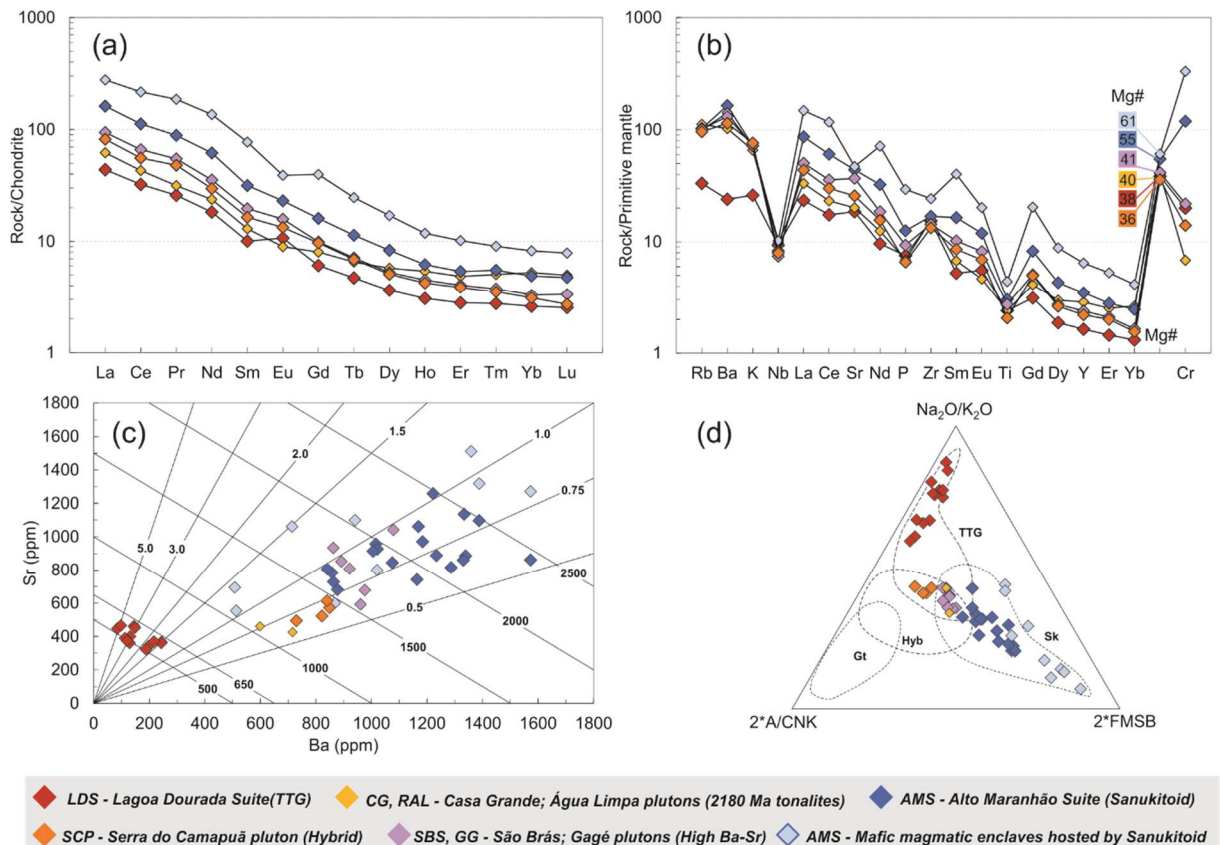


131
 132 **Figure 2:** Location of Paleoproterozoic granitoids of the Mineiro Belt in the São Francisco craton (SFC).
 133 Adapted from [Seixas et al. \(2012\)](#) and references therein. (a) The SFC in relation to the major tectonic
 134 units of South America. (b) Location of the Mineiro Belt within the southern SFC. (c) Sampling localities
 135 investigated in this study.

136 The Mineiro Belt represents a juvenile Palaeoproterozoic crustal segment
 137 ([Teixeira et al., 2015](#); [Moreira et al., 2018](#) and references therein). Its west sector, which
 138 comprises more than 6000 km² of crust almost unaffected by a younger Neoproterozoic

139 orogeny, is in stark contrast to the rest of the Palaeoproterozoic crust in the region,
140 shown in [Figure 2b](#) as orthogneisses. These chronologically-correlated segments to the
141 east - the Juiz de Fora and Mantiqueira complexes - were intensely overprinted by
142 metamorphism up to granulite facies with voluminous partial melting in the
143 Neoproterozoic (e.g. [Heilbron et al., 2017](#)). Therefore, distinguishing the
144 Palaeoproterozoic features in those terranes is inevitably hampered by the
145 Neoproterozoic orogenic overprint, which makes the relatively unaffected Mineiro Belt a
146 regional reference for geological investigation and extrapolation to the more deformed
147 terranes. Moreover, the Mineiro Belt contains both TTG and sanukitoid suites,
148 respectively known as the Lagoa Dourada suite ([Seixas et al., 2012](#)) and the Alto
149 Maranhão suite ([Seixas et al., 2013](#)). Together, they are comparable to and can be
150 categorised as most other Archaean TTG to sanukitoid transitions in many cratons
151 worldwide (e.g. [Halla et al., 2017](#); [Laurent, et al., 2014](#)). Their characteristic elemental
152 geochemistry is summarised in [Figure 3 \(a-d\)](#). All studied granitoids have intermediate
153 SiO₂ and show relative HREE depletion with absent to positive Eu anomalies (enclaves
154 sometimes show 'false negative' Eu anomalies generated by abundant middle-REE-rich
155 minerals - [Seixas et al., 2013](#)). The Lagoa Dourada Suite shows depletion of LILE, and
156 plots in the TTG field from [Laurent et al. \(2014\)](#) (red diamonds - [Fig. 3](#)). The sanukitoids
157 (SiO₂ = 60 to 66 wt.%) and hosted mafic co-magmatic enclaves (SiO₂ = 48 to 55 wt.%)
158 have the highest content of Ba+Sr, Cr and Mg# among the magmas studied (dark and
159 light blue diamonds, respectively - [Fig. 3](#)). Previous work using zircon Hf isotope and
160 whole-rock Nd isotope model ages demonstrates that these two suites have sources
161 extracted from the mantle between 2.50 and 2.45 Ga ago which evolved isotopically
162 towards 2.0 Ga ([Moreira et al., 2018](#)). These authors conclude that the metasomatism of
163 the mantle wedge generating the sanukitoid suite was caused by TTG melts such as the

164 Lagoa Dourada suite (Seixas et al., 2013), in the same way as in other cratons worldwide
165 (Moyen and Martin, 2012). In addition to the sanukitoids, a related high Ba-Sr suite (Fig.
166 3) is thought to have formed by later fractional crystallisation and/or melting of the
167 region above the mantle wedge (Moreira et al., 2018), on the basis of slightly higher SiO₂
168 content (67 wt.%) and depletion in compatible elements (pink diamonds - Fig. 3). A
169 contemporaneous pluton has lower Ba+Sr content, Mg# and Cr; and plots in the hybrid
170 field of Laurent et al., (2014) (orange diamonds - Fig 4). The Mineiro Belt also contains
171 collision-related granitoids (Teixeira et al., 2015), metavolcanics/sedimentary
172 sequences deposited at 2.088 ± 0.012 Ga (Ávila et al., 2014) and less abundant
173 granitoids derived from Archaean mafic sources, crystallized between 2.18 and 2.2 Ga
174 (Moreira et al., 2018) (yellow diamonds - Fig. 3). A volcanic to sub-volcanic unit, the
175 Serrinha-Tiradentes suite (Ávila et al., 2014), marks an important period of juvenile
176 accretion at 2.23 to 2.22 Ga along with a syn-sedimentation volcanoclastic sequence
177 deposited on top of the São Francisco palaeocraton hinterland, known as the Sabará
178 Group. The Sabará Group contains detrital zircons aged between 2.1 and 2.3 Ga with
179 juvenile signatures ($\varepsilon_{\text{Hf}(t)} > 0$) and the youngest grains indicate a maximum depositional
180 age of 2.125 ± 0.004 Ga (Martínez Dopico et al., 2017 and references therein).
181 Importantly, not only the late TTG-sanukitoid transition, but the detrital zircon grains
182 found by Martínez Dopico et al. (2017) are attributable to a period otherwise known as a
183 'tectono-magmatic lull' due to the relative scarcity of global magmatism in the geological
184 record (Spencer et al., 2018). Thus, understanding the tectono-magmatic evolution of
185 the Mineiro Belt has important global implications and also brings new insights into
186 continental crust evolution and the development of plate tectonics.



187
 188 **Figure 3:** Geochemical parameters selected from the investigated samples. (a) REE normalized to C1
 189 chondrite (Taylor and McLennan, 1985). (b) Pattern of trace elements normalized to the primitive mantle
 190 (Sun and McDonough, 1989). Note in this diagram the introduction of the non-normalized values of the
 191 parameters $100 * Mg \# [= 100 * mol MgO / MgO + 0.9 * Fe_2O_3]$ and Cr (ppm); (c) Ba versus Sr diagram,
 192 with the isovalue lines of the Sr / Ba (0.5 to 5.0) and Sr + Ba (500 to 2500 ppm). (d) Ternary diagram of
 193 classification of Neoproterozoic granitoids as suggested by Laurent et al. (2014). Triangle vertices are: $2 * A$
 194 / CNK (molar $Al_2O_3 / (CaO + K_2O + Na_2O)$); Na_2O / K_2O wt.% ratio; and $2 * (FeO_t + MgO) vs (Sr + Ba)$ wt.%
 195 (FMSB). The TTG, Sk, Hyb and Gt fields designate TTG, sanukitoids, hybrid granitoids and granitic (s.s.)
 196 suites respectively. Plots in (a) and (b) are arithmetic mean values, LDS suite (n = 12, data from Seixas et al.,
 197 2012); AM suite, tonalite host (n = 15, data from Seixas et al., 2013); AM suite, MME (dioritic mafic
 198 magmatic enclaves, n = 9, data from Seixas et al., 2013); RAL suite (n = 1, from Moreira et al., 2018); High
 199 Ba-Sr suite, n = 3, from Moreira et al., 2018); Hybrid suite, n = 3, from Moreira et al., 2018). In (c) and (d)
 200 all data from these suites of the articles by Seixas et al., 2012;2013 and Moreira et al., 2018 are included.

201 3 - Samples and Methods

202 The granitoids in this study include TTG, sanukitoid, high Ba-Sr and 'hybrid'
 203 granitoids (*sensu* Laurent et al., 2014) from Moreira et al. (2018), to which the reader is
 204 directed for a full description and detailed interpretation. The labelling scheme herein is
 205 also the same, for clarity. In addition, four metasedimentary samples, three from within
 206 the Mineiro Belt area and one from the palaeocraton domain have been analysed (Fig.
 207 2c). These samples contain detrital zircons and thus potentially represent a more
 208 comprehensive sampling of eroded equivalents to the individually-sampled granitoids

209 and their host lithologies. The samples from the Mineiro Belt are metagreywackes
210 located at the centre of the belt (16-PS-03) and at its margins with the palaeocraton (16-
211 AS-01 and 16-PS-01). The fourth sample belongs to the Sabará Group and is a
212 metadiamicctite with clasts of carbonates, granitoids, quartzites, phyllites and banded
213 iron formation, ranging in size from 1 to 15 cm. In total, 387 oxygen isotope analyses of
214 unknown zircon grains were performed using the NERC Ion Micro-Probe Facility
215 (Cameca 1270) at the University of Edinburgh, Scotland prior to U-Pb and Lu-Hf
216 analyses at the University of Portsmouth, UK. At Portsmouth, a 193 nm RESOLUTION ArF
217 Excimer laser was coupled to an Analytick Jena PlasmaQuant Elite ICP-MS for the U-Pb
218 analyses; and subsequently to a Nu Plasma I MC-ICP-MS for the Hf analyses.

219 Zircon grains with U-Pb analyses more than 5% discordant were not considered
220 for interpretation due to well-known disturbances caused in oxygen and Lu-Hf isotope
221 systems. U-Pb discordance potentially implies isotopic alteration in oxygen analyses and
222 also leads to uncertainty in crystallisation age, consequently affecting the derivation of
223 accurate initial Hf isotopic ratios. Usually, these effects modify both indices ($\delta^{18}\text{O}$ and
224 $\epsilon_{\text{Hf}(t)}$) to lower values (e.g. [Valley, 2003](#); [Payne et al., 2016](#)). However, all analyses are
225 presented in supplementary material. Some of the zircon grains with enough space in
226 the compositional domain were ablated twice for U-Pb, after having been analysed for
227 oxygen. Analyses yielded the same ages within uncertainties when compared to analyses
228 previously performed in different grains from the same samples (*cf.* [Moreira et al.,](#)
229 [2018](#)). Lu-Hf analyses were then carried out on top of the previous oxygen and U-Pb
230 pits. Complete methodology, description of the sedimentary samples and analytical
231 conditions are provided in the supplementary material.

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234 **4 – Results and preliminary interpretation**

235 Table 1 summarizes the results obtained in this study. A detailed description is
 236 provided in the following paragraphs, summarized graphically in [Figure 4](#).

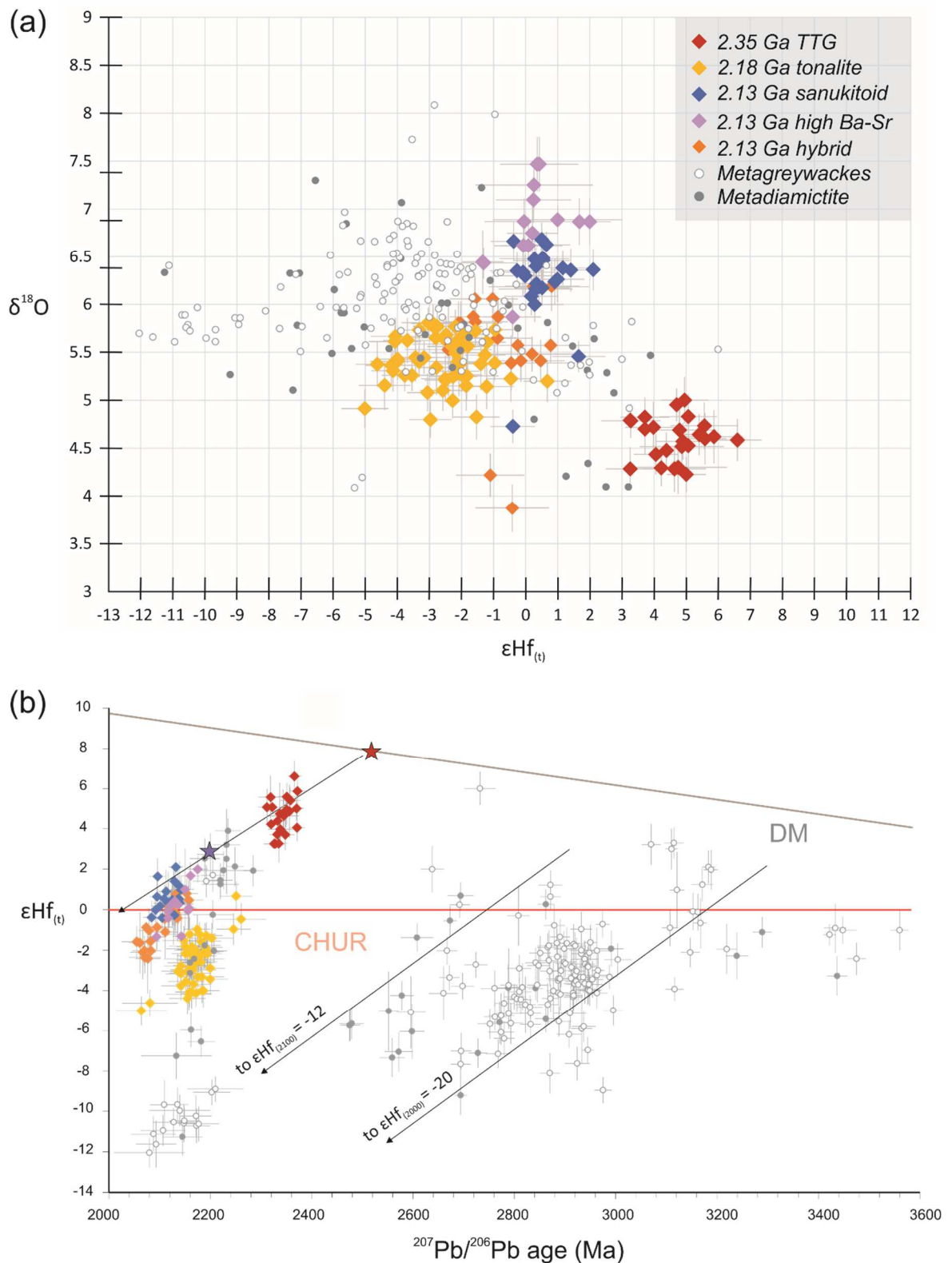
237 **Table 1:** Compilation of data obtained in this study for the igneous zircon grains. Abbreviations PS and AS
 238 stand for Palaeoproterozoic and Archaean Source, respectively. Symbols _(c) and _(r) represent analyses
 239 performed in the core or rim. Sedimentary rocks were omitted.

Sample	Suite	Age (Ga)	$\epsilon\text{Hf}_{(t)}$ (avg)	$\epsilon\text{Nd}_{(t)}$ ^a	^{Hf} T _{DM} ^a (Ga)	Nd T _{DM} ^b (Ga)	Oxygen $\delta^{18}\text{O}$ ‰ (avg)
14-LDT-01	TTG _(PS)	2.350	+3.3 to +6.6 (+4.7)	+1.0 to +2.1	2.41 to 2.61	2.4 to 2.5	+4.2 to +5.0 (+4.6)
16-MS-1D	TTG _(AS)	2.170 – 2.180	-0.9 to -4.7 (-2.7)	-2.9	2.67 to 2.93	2.6	+5.1 to +5.9 (+5.5)
14-CGT-01	TTG _(AS)	2.170 – 2.180	+0.7 to -5.0 (-2.4)	-	2.66 to 2.91	-	+4.8 to +5.7 (+5.3)
14-AMT-03	Sanukitoid	2.130	-0.4 to +1.4 (+0.5)	-1.0 to +0.9	2.45 to 2.69	2.3 to 2.4	+4.7 to +6.7 (+6.3)
16-SBS-1A	High Ba-Sr	2.130	+2.0 to -1.3 (+0.2)	+0.3	2.48 to 2.72	2.3 to 2.4	+5.9 to +7.5 (+6.8)
14-SCT-01	Hybrid	2.120 – 2.130	+0.8 to -2.4 (-0.9)	-1.2 to -0.8	2.52 to 2.77	2.5	+3.9 to +6.2 (+5.6)

240 ^a Range of values based on average of model ages after calculations using different constants (see
 241 supplementary file for details).

242 ^b Data compiled from [Seixas et al. \(2012; 2013\)](#) and [Moreira et al. \(2018\)](#).

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Figure 4: Oxygen and hafnium isotopic composition of zircons from plutonic and sedimentary rocks of the Mineiro Belt, Brazil represented in $\delta^{18}\text{O}$ (relative to VSMOW) and ϵHf notation for the diagram in panel (a) and $^{207}\text{Pb}/^{206}\text{Pb}$ age versus ϵHf in panel (b). Igneous zircons are colour-coded following figure 2. Filled grey circles are detrital zircon grains from the foreland basin meta-sediments and the open circles are detrital grains from the metagreywackes within the belt. Error bars for both diagrams are 2σ confidence level. Panel (b) shows proposed evolution lines in ϵHf -age space. Red star represents extraction from the depleted mantle (DM) and purple star represents potential mantle composition at c. 2.2 Ga. See details for DM and CHUR parameters in the supplementary material.

253 4.1 – Igneous rocks

254 4.1.1 Tonalite – trondhjemite-granodiorite suite (TTG)

255 U-Pb analyses carried out on zircon grains from the garnet-bearing high-Al TTG –
256 Lagoa Dourada suite yielded concordant ages (all > 96% concordance) with weighted
257 mean average of 2.344 ± 0.0057 Ga (MSWD = 1.1). The concordant grains have a
258 weighted average age of 2.342 ± 0.01 Ga (MSWD = 1.0). $^{176}\text{Hf}/^{177}\text{Hf}$ zircon analyses
259 record initial mean compositions that are considerably above CHUR; $\epsilon\text{Hf}_{(t)}$ values cluster
260 between +3.26 and +6.6 and average +4.65. Oxygen isotope analyses yield $\delta^{18}\text{O}$ values
261 between +4.2 and +5.0 ‰. Together, the narrow range of both values are consistent
262 with a young mafic oceanic crust source that had been altered to some extent by surface
263 processes (e.g. [Hiess et al., 2009](#)), thus modifying the O-isotope signature.

264 Tonalites of 2.18 and 2.2 Ga age contain metabasaltic xenoliths with ~3.3 Ga
265 Archaean model ages ([Seixas et al., 2013](#)). Country rock assimilation has been suggested
266 as an explanation for $\epsilon\text{Nd}_{(t)}$ values as low as -2.9 ([Moreira et al., 2018](#)). The ϵHf values
267 down to -5.0 $\epsilon\text{Hf}_{(t)}$ (average -2.6) are in agreement with the -2.9 $\epsilon\text{Nd}_{(t)}$ whole-rock
268 signature, but zircon $\delta^{18}\text{O}$ values reflect mantle derivation. Indeed, 57 out of 61 grains
269 have $\delta^{18}\text{O}$ values between $+5.1 \pm 0.21$ ‰ and $+5.9 \pm 0.15$ ‰ (average +5.5 ‰). The
270 other four grains have slightly lower $\delta^{18}\text{O}$, down to $+4.8 \pm 0.2$ ‰. Thus, it is more
271 plausible that tonalites were derived from Archaean mafic crust that resided in the
272 lower crust of the Mineiro Belt for up to 800 Myr, but with insignificant supracrustal
273 contamination which would have modified $\delta^{18}\text{O}$ towards higher values. This long
274 residence time is required to explain the Hf and Nd isotope evolution, from extraction of
275 source at c. 3.0 Ga to re-melting at 2.18 Ga.

276 4.1.2 Sanukitoids and associated rocks

277 The youngest igneous rocks of this study are c. 2.13 Ga old and are divided in to
278 three distinct groups: sanukitoids (Alto Maranhão Suite) marked by LILE enrichment
279 (specially Ba and Sr) with high Mg, Ni and Cr; high Ba-Sr granitoids with significantly
280 lower compatible elements; and hybrid granitoids rather less enriched in Ba and Sr (Fig.
281 3) and endowed with some crustal inheritance (identified by Archaean inherited zircons
282 and older model ages).

283 For the sanukitoids, eleven concordant zircons with $^{207}\text{Pb}/^{206}\text{Pb}$ age ranging from
284 2.102 ± 0.036 Ga and 2.140 ± 0.043 Ga yielded $\delta^{18}\text{O}$ values between +6.18 and +6.68 ‰
285 (average $+6.35 \pm 0.22$ ‰). Twenty-two other zircons with concordance varying from 95
286 to 103 % have $\delta^{18}\text{O}$ values between +4.7 and +6.7‰ (average +6.2 ‰). The $\epsilon\text{Hf}_{(t)}$ values
287 of the concordant zircons are essentially chondritic to slightly super-chondritic (+0.3 to
288 +1.15); the slightly discordant grains average +0.47 with some values as low as -0.4, the
289 latter likely an artefact caused by discordance (e.g. [Payne et al., 2016](#)). The oxygen
290 isotope signatures range up to +6.7‰ and likely reflect a sedimentary contribution in
291 the magma source, possibly from subduction-related enrichment of the mantle (e.g.
292 [Fowler et al., 2008](#); [Heilimo et al 2013](#)). Incorporation of supracrustal material within
293 the crust is not a viable interpretation of the high $\delta^{18}\text{O}$ values because 1) the sanukitoid
294 does not contain xenoliths of any nature, only abundant co-magmatic andesitic-basaltic
295 enclaves; 2) the whole rock $\epsilon\text{Nd}_{(t)}$ and zircon $\epsilon\text{Hf}_{(t)}$ values are essentially chondritic with
296 no evidence of interaction with older crust; and 3) older crust in the region has much
297 lower Ba-Sr content. Therefore, enrichment must have happened in the magma source.

298 The high Ba-Sr granitoids yielded $^{207}\text{Pb}/^{206}\text{Pb}$ ages ranging from 2.094 ± 0.038 Ga
299 and 2.175 ± 0.040 Ga (average of 2.136 ± 0.034 Ga) and $\delta^{18}\text{O}$ values between +5.9 and
300 +7.5 ‰ (average +6.8 ‰). The $\epsilon\text{Hf}_{(t)}$ values vary from -1.3 to +2.0 and therefore closely

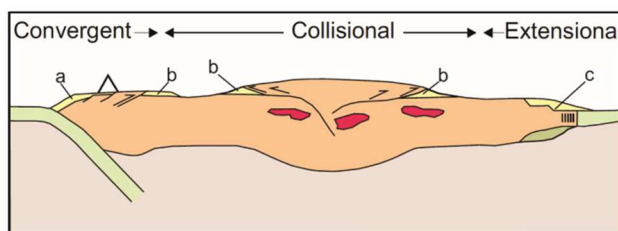
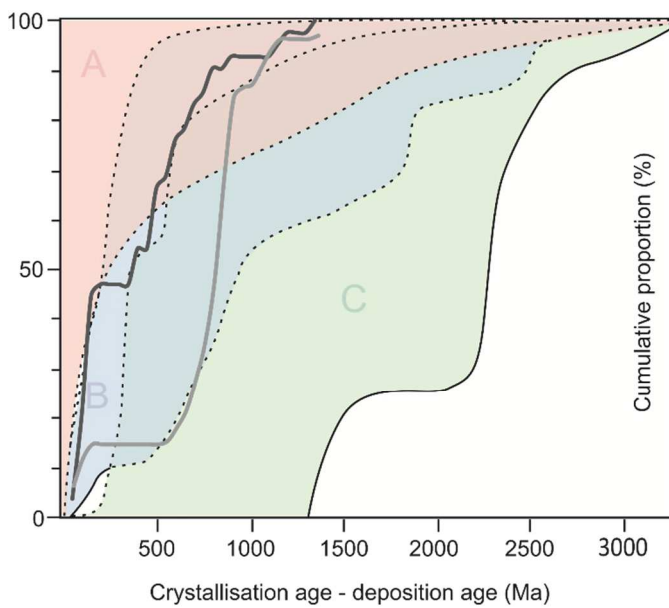
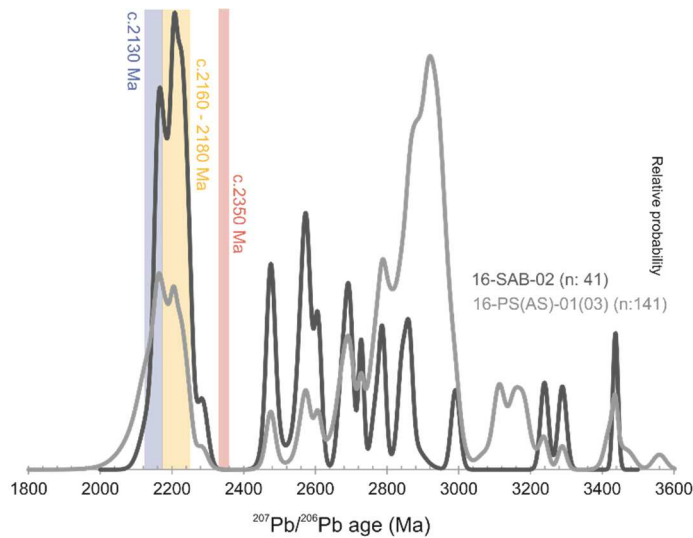
301 overlap those of the sanukitoids. Since they have only marginally higher $\delta^{18}\text{O}$ a genetic
302 link is possible, perhaps via fractional crystallisation of the same or similar magma. The
303 third group (hybrid granitoids) yielded zircons ages between 2.061 ± 0.046 Ga and
304 2.158 ± 0.037 Ga and $\delta^{18}\text{O}$ values between $+3.9 \pm 0.25$ and $+6.18 \pm 0.26$ ‰ (average $+5.6$
305 ‰) with no clear relationship between age and oxygen isotope signature. The $\epsilon\text{Hf}(t)$
306 values are distinctly more negative than the first two groups, ranging from $+0.8$ to -2.4
307 with the least radiogenic signatures (i.e. lower $\epsilon\text{Hf}(t)$) in the youngest grains.

308 *4.2 – Sedimentary rocks*

309 Detrital zircon grains from metagreywacke samples have a general bimodal age
310 distribution in probability histograms with ages varying from 2.080 to 3.560 Ga. The
311 main peak is around 2.9 Ga and the youngest subordinate peak is around 2.1 Ga (Fig.
312 5a). The meta-diamictite has a similar range of detrital zircon ages, but the distribution
313 is distinct: the highest peak is around 2.1 Ga and there are several smaller peaks as old
314 as 3.3 Ga. The three metagreywacke samples were deposited in an extensional/passive
315 margin setting identified by the higher proportion of Archaean inheritance compared to
316 the maximum depositional age of 2.090 Ga (see supplementary material for explanation
317 on the maximum depositional age) (Cawood et al., 2012) (Fig. 5). Thus, the lack of
318 significant inheritance in the plutonic rocks of the belt contrasts significantly with the
319 detrital zircon spectra. This can be explained either by complete melting of xenocrystic
320 zircons in high temperature magmas, little contamination or zircon-absent local crust
321 during emplacement. The latter would imply that the Archaean detrital zircon grains
322 come from the SFC to the north and the crust traversed and intruded by the granitoids
323 was predominantly mafic.

324 The sample collected from the Sabará Group in the palaeocraton domain shows a
325 typical foreland-type detrital zircon spectrum (Fig. 5). Zircon grains with ages close to
326 the 2.2 Ga volcanic arcs in the region (Ávila et al., 2014) are mostly juvenile according to
327 the Hf and oxygen isotopes (averages $\epsilon\text{Hf}_{(t)}$ and $\delta^{18}\text{O}$ for c. 2.2 Ga grains are +2.3 and
328 +4.9 ‰, respectively). The grains with ages close to the maximum depositional age (c.
329 2.125 Ga) have $\delta^{18}\text{O}$ values averaging 5.9 ‰ and $\epsilon\text{Hf}_{(t)}$ as low as -7. Archaean secondary
330 peaks correlate to the palaeocraton sources (e.g. Teixeira et al., 2015). Strikingly, the
331 oxygen and hafnium isotopic compositions of the detrital zircons do not overlap with
332 most of the igneous zircons. This suggests that these igneous rocks were absent from the
333 sedimentary provenance. Moreover, $\delta^{18}\text{O}$ values up to 8‰ together with ϵHf values
334 down to -12 indicate recycling of the crust during the Archaean. Archaean growth
335 episodes are more prominent at c. 3.0 Ga, where detrital zircon grains have super-
336 chondritic ϵHf and $\delta^{18}\text{O}$ values compatible with mantle melts (Fig. 4).

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338

339 **Figure 5:** Probability density distributions of the detrital zircon ages show three main characteristics: 1)
 340 Several older age peaks have no correspondence with magmatic events in the Mineiro Belt; 2) Largest
 341 contribution of ages are different in the two sedimentary units of this study; 3) Detrital zircon grains do
 342 not record age peak within the c. 2.35 Ga TTG magmatic event interval. Diagram from [Cawood et al.](#)
 343 [\(2012\)](#) shows cumulative proportion curves of the crystallisation age of the detrital zircon grains minus
 344 the deposition age of the sedimentary unit on x-axis. The diagram indicates the tectonic settings in which
 345 the sediments were deposited, for which A, B and C fields on the diagram relate to a, b and c on tectonic
 346 cartoon. The metagreywackes plot towards the extensional/passive margin field (grey curve), whereas
 347 the syn-orogenic metasedimentary rock plots on the convergent/collisional foreland basin field (black
 348 curve). Metagreywackes from the belt have a higher contribution of Archaean grains compared to the
 349 maximum depositional age at 2.09 Ga. The detrital zircon distribution for this sample contrasts drastically
 350 to the zircon ages in the plutonic rocks, which suggests distant cratonic areas as the main sources for the
 351 passive margin basin.

352 **5 – Discussion**

353 *5.1 – TTGs and sanukitoid magma generation*

354 Most TTGs are derived from mafic rocks, themselves derived from undepleted
355 mantle and comprise the majority of intermediate Archaean igneous rocks (e.g. [Moyen
356 and Laurent, 2018](#)). Nonetheless, superchondritic zircon grains derived from TTGs are
357 reported in this study and in other occurrences worldwide, indicating a depleted mantle
358 source (see also [Fig. 4](#)). Hydration and alteration of the mafic source seems to be a
359 fundamental prerequisite, but they could be derived from mafic oceanic plateaus ([Hastie
360 et al., 2016](#)), in a shallow subduction style ([Moyen and Martin, 2012](#)) or in a thickened
361 mafic crust (e.g. [Smithies, 2000](#)). The melting conditions of the mafic sources range
362 significantly, from below 10 to more than 25 kbar, which yields a large pressure-
363 dependent mineralogical range of residues during and after TTG-melt extraction ([Foley
364 et al., 2003](#)), and therefore results in significant trace element variation ([Moyen and
365 Martin, 2012](#)). Conversely, [Laurent et al. \(2020\)](#) have recently proposed that this whole
366 geochemical variation can be a result of crystal-fractionation of a single tonalitic source
367 formed by basaltic melting or differentiation in the lower crust (at <40 km depth). A
368 broadly-chondritic reservoir is a consistent source for the generation of most TTGs,
369 because an undepleted mantle is likely to melt more easily than any subsequent
370 depleted mantle reservoir (e.g. [Moyen and Laurent, 2018](#)). As such, depleted mantle
371 continues to grow at the expense of more primitive mantle ([Moyen and Laurent, 2018](#))
372 and it has been suggested that exhaustion of the latter coincides with the proposed ca.
373 2.4 – 2.2 Ga magmatic lull ([Spencer et al., 2018](#)). Therefore, TTG and sanukitoid
374 generation in the Mineiro Belt could represent the global 'last gasp' of this transitional
375 magmatism.

376 As outlined above, the enrichment in LILE (especially Ba and Sr) alongside the
377 characteristic high Mg#, Cr and Ni of sanukitoids require at least two end-members: an
378 ultramafic component has somehow to be enriched in LILE by the second component
379 (e.g. [Smithies, 2000](#)). Sanukitoids are commonly thought to derive from the interaction
380 between a TTG-like melt (\pm sediments) and mantle peridotite ([Martin et al., 2009](#);
381 [Moyen and Martin, 2012](#)), but there are many variations upon that theme. A lack of or
382 small positive Eu anomaly associated with Sr enrichment suggests the absence of
383 plagioclase in the residue and hence a deeper source ([Moyen and Martin, 2012](#)).

384 Some of the tectonic mechanisms proposed that are consistent with these
385 constraints include dehydration and melting of a subducted oceanic slab (e.g. [Fowler et](#)
386 [al., 2008](#)), slab break-off ([Halla et al., 2009](#)), and/or two-stage metasomatisation with
387 mantle upwelling and delamination of the subcontinental lithospheric mantle ([Heilimo](#)
388 [et al., 2010](#)). Each could explain the origin of specific magmas, but the latter attempts
389 also to explain the paradox of magmas with similar geochemical characteristics but
390 different isotopic signatures. The model explains, for example, the reason why magmas
391 with a sediment contribution may not have enriched $\epsilon_{\text{Hf}}/\epsilon_{\text{Nd}}$ composition, and predicts
392 an explanation for a major element distinction between low and high-Ti sanukitoids,
393 based on modelling between degree of melting and enrichment of the source ([Martin et](#)
394 [al., 2009](#)). Similarly, [Laurent et al. \(2014\)](#) regard aspects of crustal reworking as markers
395 of sanukitoid generation through time, because increasingly negative ϵ_{Nd} and ϵ_{Hf}
396 isotopic features can be a consequence of old sediment intake into the mantle wedge.
397 Notwithstanding these details, given the geochemistry, broadly-chondritic ϵ_{Hf} and
398 generally high $\delta^{18}\text{O}$ values of the 2.13 Ga plutonic rocks from the Mineiro Belt, they
399 probably interacted with a mantle wedge at some point in their history. This hypothesis

400 is tested and constrained with a novel three-component Hf-O isotope mixing model,
401 discussed below.

402 *5.2 – A zircon-based mixing model between mantle, TTG-melt and sediments*

403 Zircon grains that grew in equilibrium with mantle melts retain a $\delta^{18}\text{O}$ isotopic
404 signature at around $5.3 \pm 0.6\text{‰}$ (Valley, 2003). Those that crystallised from magmas
405 with variable incorporation of supracrustal material will have a proportionally higher
406 $\delta^{18}\text{O}$ (e.g. Hopkinson et al 2017), since oxygen isotopes fractionate strongly under low-
407 temperature surficial processes due to the large positive mineral-water fractionation
408 factors at low temperature (Zheng, 1993). Conversely, high-temperature hydrothermal
409 activity ($T > 400^\circ\text{-}500^\circ\text{C}$) may modify $^{18}\text{O}/^{16}\text{O}$ to lower $\delta^{18}\text{O}$ during alteration of oceanic
410 crust at deeper levels (>2.5 km) (Gregory and Taylor, 1981). This is because at high T,
411 mineral-water fractionation factors are low so that interaction with seawater ($\delta^{18}\text{O} = 0$)
412 is able to produce rock values lower than those of the mantle (Zhao and Zheng, 2003).
413 Hafnium isotope model ages may be used to estimate protolith separation age from a
414 mantle reservoir, and the combination of both is a powerful tool in crustal evolution
415 research (e.g. Kemp et al., 2006; Dhuime et al., 2018 and references therein). For
416 example, reworking arrays sometimes generated by regional data (when they show
417 similar regression towards the mantle reservoir) may represent major crustal growth
418 events, within which oxygen isotopes can help constrain the juvenile contribution.
419 Although there is an increasing debate about model ages (Payne et al., 2016 and
420 references therein), the applicability of the approach alongside accurate U-Pb zircon
421 ages, to constrain evolved versus juvenile signature in ϵHf -time space, is not in doubt.

422 In this study, oxygen isotopes do not correlate clearly with most whole-rock
423 parameters. However, the samples with the highest Ba plus Sr content have the highest

424 $\delta^{18}\text{O}$, which points to a probable sedimentary contribution (Laurent et al., 2011). In
425 order to better understand the variations presented by the Hf and O isotopes, we have
426 constructed a concentration-weighted ternary mixing model showing the possible
427 results of crustal assimilation by mantle-derived melts (Fig. 6a). The model incorporates
428 proportions of mixing with end members of variable concentrations, and thus results in
429 arcuate-bounded regions in a ternary mixing model diagram. End-members we consider
430 are (1) the mantle (less depleted mantle at c. 2.2 Ga; see implications below), (2) the
431 average composition of a TTG-melt derived from a high-T-altered oceanic crust ($T_{\text{DM}} = \sim$
432 2.5 Ga), and (3) three sediments of different ages. Parameters used are listed in Table 2.
433 The ratios between the 2.2 Ga mantle and the crustal components (Hf_M/Hf_s) are 0.067
434 given the Hf concentration of the mantle (0.3 ppm – Stille et al., 1986) and the average Hf
435 concentration of Palaeoproterozoic sediments (~ 4.5 ppm); and 0.075 given the same
436 mantle composition and the average Hf concentration of Archaean sediments (~ 4 ppm)
437 (Vervoort et al., 1999). For mixing between the sediments and TTG-melt the Hf_s/Hf_{TTG}
438 ratio is 0.9, and between the mantle and TTG-melt the ratio is 0.06 (Hf_M/Hf_{TTG}). Each
439 proposed sediment end-member is modelled separately in combination with the other
440 two end-members (i.e. TTG-melt and mantle), yielding three trianguloid areas (Fig. 6 b,
441 c, d).

442 The modelling particularly addresses the composition of sanukitoid magmas
443 given their well-known complexity outlined above. Sediment composition is a strikingly
444 sensitive petrogenetic control because of its higher Hf concentration and elevated $\delta^{18}\text{O}$
445 isotopic signature. Successful models (passing close to sanukitoid compositions) were
446 obtained from both Palaeoproterozoic sediment end-members (Fig. 6b triangles 1,2 and
447 6c triangles 5,6), but the Archean model was implausible (Fig. 6d). Of the
448 Palaeoproterozoic possibilities, the ‘self-feeding arc’ (sediment 1), in which sediments

449 derive from the arc itself, represents the best explanation for the sanukitoid magmas,
 450 because sediment 2 would require a mixture with insufficient mantle/too much TTG
 451 input, inconsistent with bulk geochemical characteristics.

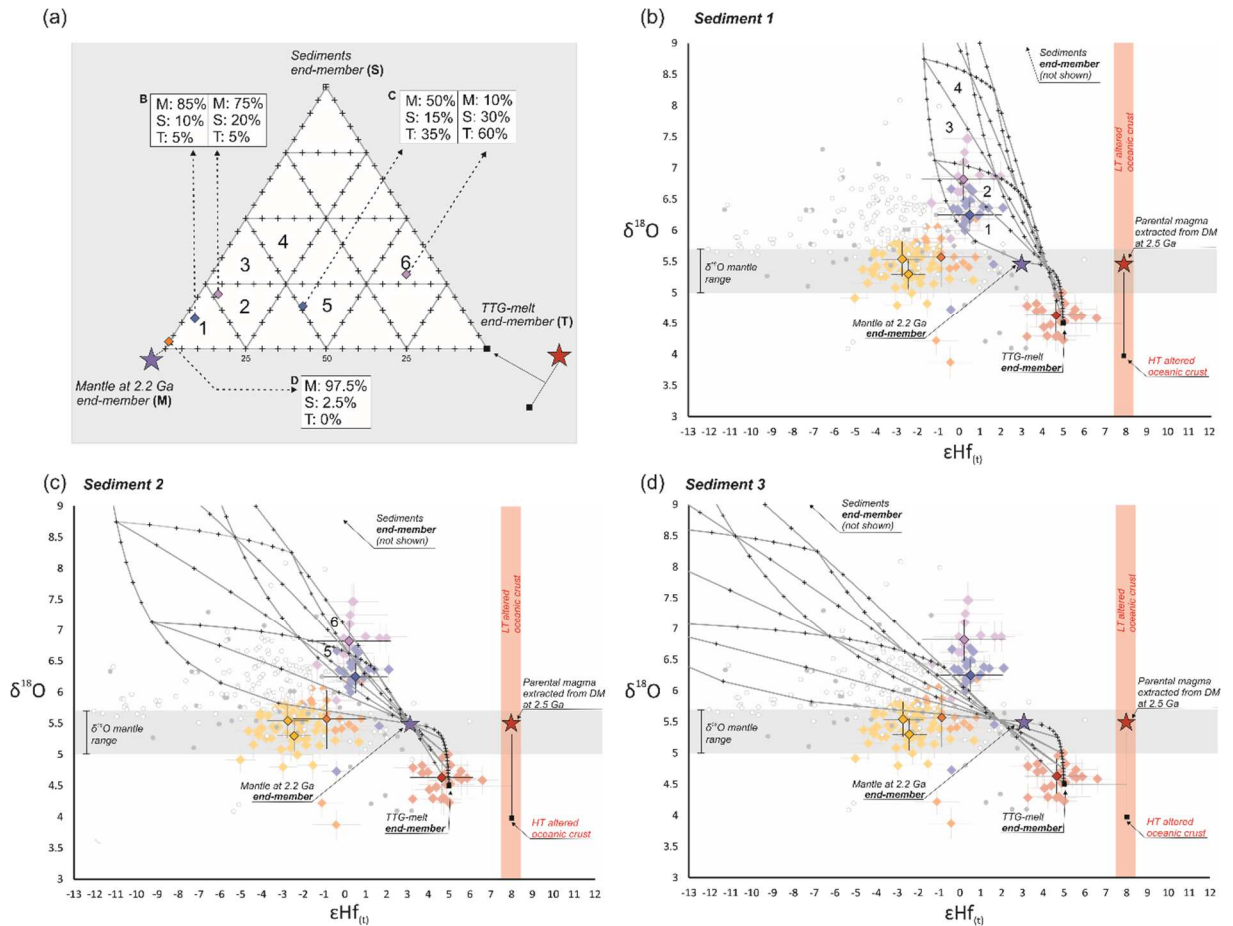
452 **Table 2:** Possible reservoirs and estimations for $\epsilon\text{Hf}(t)$ values, O isotope composition and Hf concentration
 453 used in the ternary mixing diagrams. The three mixing ternary areas differ only by the sediment source
 454 (i.e. Archaean or Palaeoproterozoic).

Reservoir	$\epsilon\text{Hf}(t)$	Reasoning	$\delta^{18}\text{O}$ (‰)	Reasoning	Hf (ppm)	Reference
Depleted mantle at 2.5 Ga	8	Intercept with the DM line (red star)	5.5	Equilibrium with mantle melts during extraction Valley (2003)	0.157	Workman and Hart (2005)
2.2 Ga mantle	3	Intercept between crustal array and mantle evolution line (purple star)	5.5	Equilibrium with mantle melts during extraction Valley (2003)	0.3	Stille et al. (1986)
TTG-melt	5	Average of Hf isotopes analysed in this study for LDS	4.5	High-T altered mafic source mix with unaltered mafic source	5	Seixas et al. (2012) – highest concentration
Sediment 1 (Palaeoproterozoic)	-2	Hypothetical sediment derived from the own arc (average $\epsilon\text{Hf}(t) = 0$) with little evolved signature	12	Shieh and Schwarcz (1978)	4.5	Vervoort et al. (1999) – average of juvenile sediments
Sediment 2 (Palaeoproterozoic)	-12	Lowest signature of c. 2.1 Ga detrital zircon grains (high evolved signature)	12	Shieh and Schwarcz (1978)	4.5	Ditto
Sediment 3 (Archaean)	-20	Hypothetical sediment derived from evolved crust (CHUR at 3 Ga)	12	Shieh and Schwarcz (1978)	4	Vervoort et al. (1999) – average of Archaean sediments

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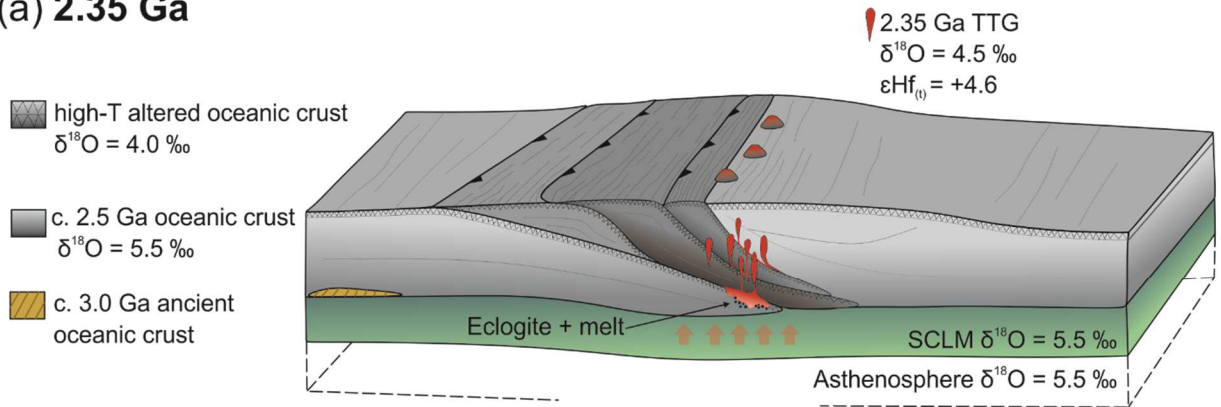
Figure 6: Zircon-based ternary mixing models and ϵHf versus $\delta^{18}\text{O}$ diagrams. Dark grey lines show the mixing between mantle-derived magmas, TTG-melts and sediment end-members (see methodology for constants and estimations applied). Each black cross in these curves represents a 5% interval between the end-member compositions. (a) Hypothetical triangle for elucidation of the modelling. It represents ternary mixing from which the reservoirs are equally distant and have the same Hf concentrations. Average of the zircon grains analysed for each of the suites of rocks are plotted in this diagram to show how the estimation of the constituents were determined, respectively for models in (b), (c) and (d). Sub-triangular domains presented in (a) are also located in diagrams (b) and (c) for comparison. (b) Modelling based on sediments 1 from table 2. (c) Modelling based on sediments 2 from table 2. (d) Modelling based on sediments 3 from table 2.

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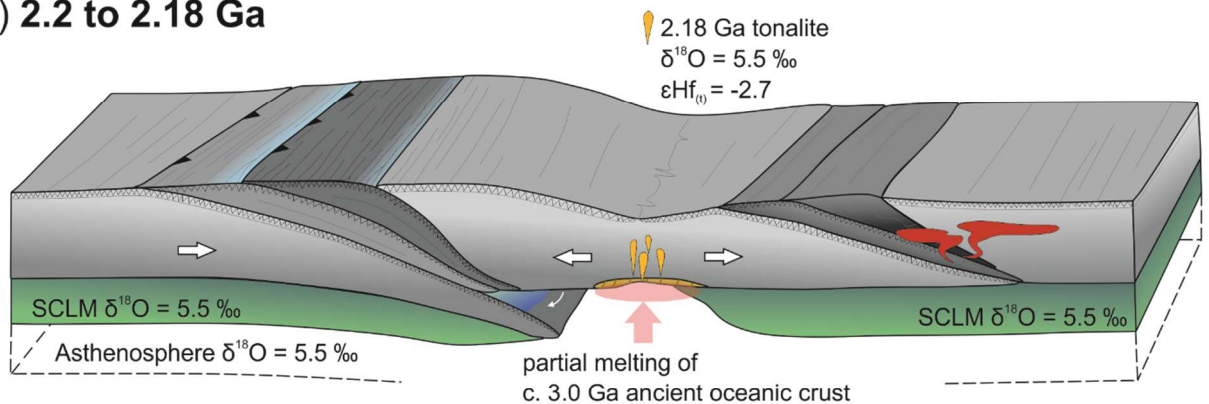
470 Although based on approximations of global sedimentary rocks, the modelling is
 471 consistent with accepted models of TTG generation, and provides convincing evidence
 472 for sediment contamination of mantle melts in sanukitoid petrogenesis. Extending the
 473 model to a plausible tectonic explanation, we have distinguished 3 chronological stages

474 (Fig. 7).

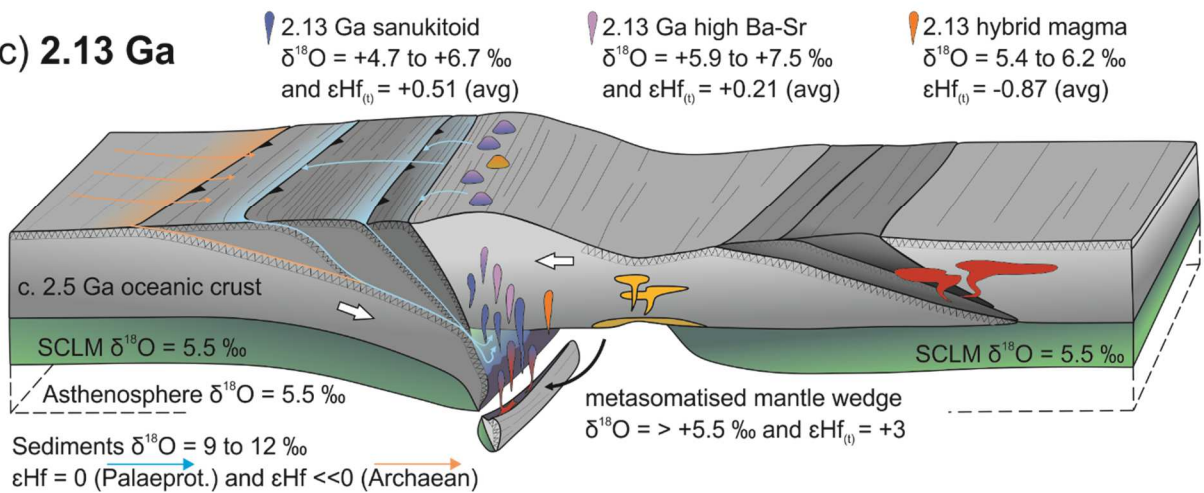
(a) 2.35 Ga



(b) 2.2 to 2.18 Ga



(c) 2.13 Ga



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Figure 7: Tectonic model conceived for steepening of subducted oceanic slab due to TTG-magma generation and eclogite residue (not to scale). (a) Melting of a mixture of altered and pristine oceanic crust generates the TTG magmas and eclogitization of the under plate. (b) Steepening of the plate and initiation of the mantle wedge at c. 2.2 Ga. Consequently, a 'back-arc' type basin triggers re-melting of older Archaean mafic crust in the lower crust at c. 2.18 Ga. (c) Sediments driven from the subducted plate metasomatise the mantle and mix with small portions of the TTG-like magmas to generate the sanukitoids and high Ba-Sr magmas by fractional crystallisation at 2.13 Ga. Hybrid granitoid (and to a certain extent the high Ba-Sr magmas) generation involved participation of small amounts of Archaean sediments.

487 *Stage 1: Palaeoproterozoic-derived TTG*

488 In the model, the tonalites are derived from a high-T-altered mafic crust with
489 $\epsilon\text{Hf}_{(t)}$ composition of +8 and $\delta^{18}\text{O}_{\text{WR}}$ of 4 ‰ (Eiler, 2001). This source is consistent with
490 a tholeiitic mantle magma extracted at 2.5 Ga, altered on the sea-floor by high-
491 temperature waters and shortly after melted to generate the existing 2.35 Ga tonalites.
492 There is also the possibility of mixing melts from different mafic sources with different
493 degrees of hydrothermal alteration. By mass balance, a mixture of 60 % of altered mafic
494 crust ($\delta^{18}\text{O}_{\text{WR}} = 4$ ‰) and 40 % of unaltered mafic crust ($\delta^{18}\text{O}_{\text{WR}} = 5.5$ ‰) would
495 generate zircon grains in the tonalite with $\delta^{18}\text{O}$ of 4.6 ‰.

496 *Stage 2: Archaean-derived tonalites*

497 Hf isotopes of the c. 2.180 Ga suite yielded the oldest model ages for the plutonic
498 rocks of this study (c. 3.0 Ga). However, mantle-derived $\delta^{18}\text{O}$ values and less evolved
499 geochemical features (low SiO_2 , K, Ba, and Sr) suggest minor supracrustal contribution.
500 Based on the superposition of negative $\epsilon\text{Nd}_{(t)}$ values of sample 16-MS-1D and the Nd
501 evolution line of one of the amphibolite rafts within the main tonalite (Seixas et al.,
502 2012), Moreira et al. (2018) suggested that crustal melting occurred during the
503 formation of the tonalite at 2.180 Ga, as assimilation of an Archaean mafic crust could be
504 linked to the presence of amphibolite xenoliths. Alternatively, the rafts could represent
505 portions of a mafic source not completely consumed by the derived tonalitic melt. One
506 way to identify how much of this Archaean mafic crust was involved is modelling the
507 $\delta^{18}\text{O}$ and Hf composition from the depleted mantle towards the $^{176}\text{Hf}/^{177}\text{Hf}$ composition
508 of the zircons from the tonalite. The ternary mixing model (Fig. 6) shows that sediments
509 or old crust did not contribute significantly to the tonalite composition, which seems to
510 have been dominated by a modelled magma with $\epsilon\text{Hf} \sim +6.5$ units and $\delta^{18}\text{O} \sim 5$ ‰.

511 Therefore, melting of an unaltered Archaean mafic source better explains the isotopic
512 signatures and implies a quiescent residence time of roughly 800 Myr. One tectonic
513 scenario for the genesis of such tonalites involves lithosphere thinning and
514 asthenosphere upwelling during roll-back of a subducting plate, resembling a back-arc
515 basin (Fig. 7b). This would provide sufficient heat for crustal melting and could have
516 occurred shortly after the mantle-wedge initiation suggested to have occurred at 2.2 Ga
517 (see below).

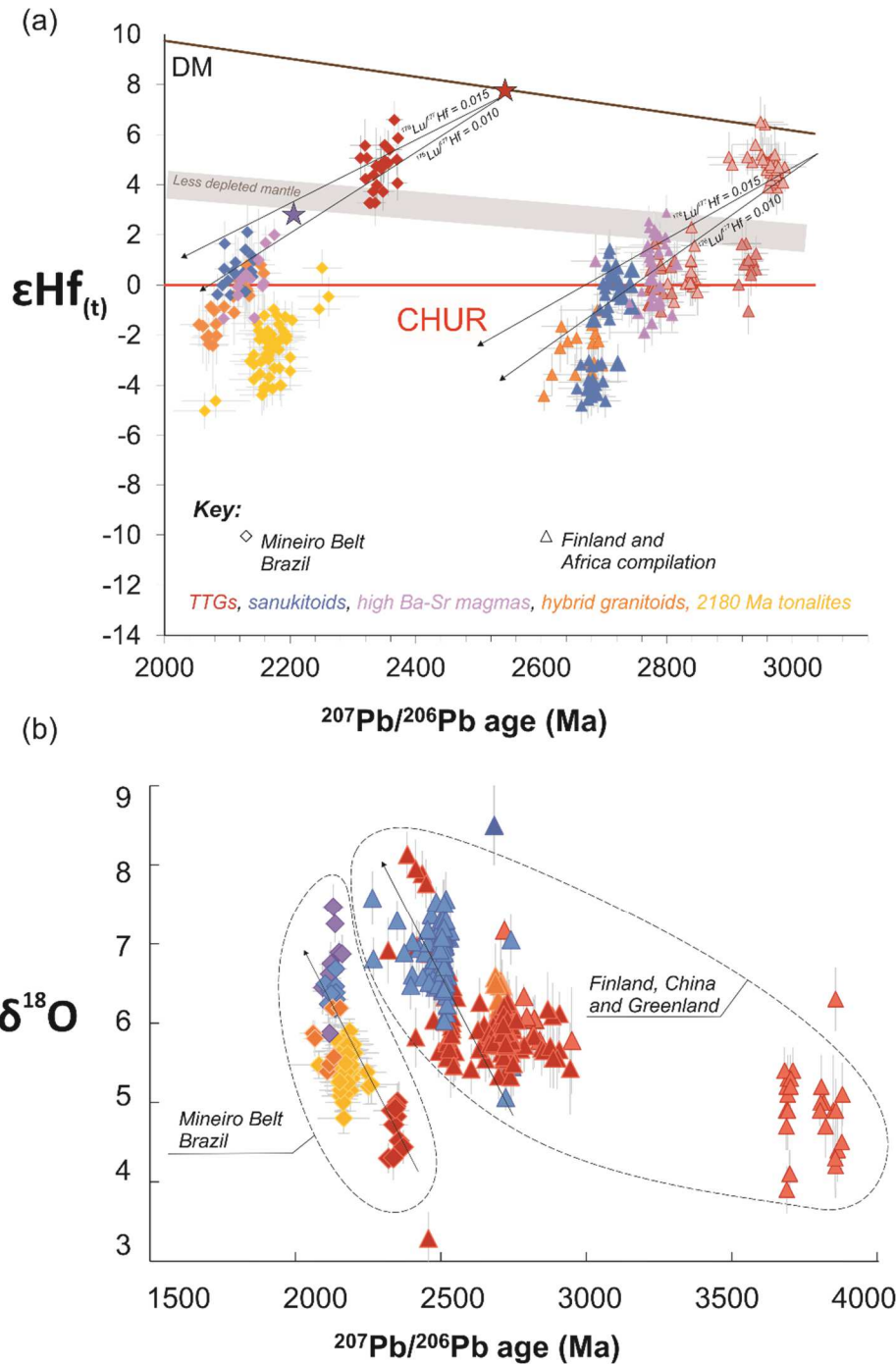
518 *Stage 3: Sanukitoids, high Ba-Sr magmas and hybrid granitoids*

519 Sanukitoids and high Ba-Sr magmas show evidence for mantle interaction with a
520 TTG-like melt and/or sediments (e.g. Martin et al., 2009; Laurent et al., 2011, Fowler et
521 al., 2008). The model presented here uses a mantle component with $\epsilon_{\text{Hf}} = +3$ and $\delta^{18}\text{O} =$
522 5.5‰ . This is justified by the better fit in the crustal evolution array lines in ϵ_{Hf} versus
523 time space (Fig. 4 and 8) and the overlap with a less-depleted mantle evolution line
524 (based on Hf isotopes of deep-mantle plumes, Stille et al., 1986). Following the mantle
525 wedge hypothesis for sanukitoid derivation, this is consistent with proto-subduction
526 starting at c. 2.2 Ga, whereby the incremental density of eclogite residue at the base of
527 the crust reached the 'tipping point', and this dense material foundered into the mantle
528 (e.g. Bédard et al., 2018). Then, seventy Myr later a mantle wedge had formed from which
529 the sanukitoid magmas were derived at 2.13 Ga. As soon as weathering and erosion of
530 the developing arc started, the derived ^{18}O -enriched sediments were promptly recycled
531 back in to the mantle, retaining a relatively juvenile Hf signature. Therefore, the ϵ_{Hf}
532 signature of the sediments used for the model is set at -2 (lowest possible value – taking
533 into account uncertainties – obtained in igneous zircon for the sanukitoid/high Ba-Sr
534 magmas). This process can be described as self-feeding of the arc, indicated by

535 increasing $\delta^{18}\text{O}$ values from 4.7 ‰ to 7.5 ‰. Ternary modelling implies the precursor
536 magma was extracted from a portion of the mantle wedge modified by c. 10 to 20% of
537 subducted sediments (Fig. 6b and Fig. 7). Most of the constituents are mantle-derived
538 (85 and 75% for sanukitoid and high Ba-Sr granitoids respectively) with only 5 to 10 %
539 derived from TTG-like melts. Alternatively, using a contemporary mantle at 2.13 Ga with
540 chondritic signature, the modelling yields c. 5% lower mantle contribution to the
541 magmas, but maintain the secondary role of the sediments and TTG components (see
542 supplementary material). The proportion of sediments calculated to be involved in the
543 sanukitoid composition with realistic model ages does not change for the two different
544 mantles used in the model (i.e. 2.2 or 2.13 Ga mantle), which has implications for the
545 composition of the sedimentary sources undergoing exhumation and erosion at low
546 temperatures.

547 A special case is shown by the zircons from trondhjemites and granodiorites of
548 the hybrid granitoid pluton, originally incorporated in the high Ba-Sr Suite by [Moreira et](#)
549 [al. \(2018\)](#). The pluton has lower Mg# and Ba + Sr + Fe concentration compared to the
550 other granitoids of the high Ba-Sr Suite, and straddles the hybrid granites field of
551 [Laurent et al. \(2014\)](#) (Fig. 3d). The dispersion towards more negative ϵ_{Hf} values in the
552 ternary modelling and overall older T_{DM} ages (for both Hf and Nd isotopes) suggest a
553 small contribution from older Archaean sediments. The overlap of the $\delta^{18}\text{O}$ versus ϵ_{Hf}
554 space of the detrital Archaean zircons presented here supports this hypothesis (Fig. 4d).

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557 **Figure 8:** Comparison of (a) Hf and (b) oxygen isotopes of zircon grains from TTG-sanukitoid and
 558 comparable magmas worldwide (Zeh et al., 2009; 2013; Heilimo et al., 2011; 2013) and the Mineiro Belt.
 559 Black arrows in (a) represent plausible crustal reservoirs ($^{176}\text{Lu}/^{177}\text{Hf} > 0$) and point to similar evolution
 560 arrays regardless of the eon in which they occur. The colour codes match the following lithotypes: red for
 561 TTG, blue for sanukitoids, pink for high Ba-Sr magmas and orange for hybrid magmas. The
 562 Palaeoproterozoic zircon grains in diamond shapes represent analyses from the Mineiro Belt, and the
 563 triangles are from localities in Finland and Africa. They project similar crustal evolution arrays through
 564 time, regardless of their age. Oxygen isotope analyses from Archaean zircon grains from Finland, China
 565 and Greenland (Hiess et al., 2009; Mikkola et al., 2011; Heilimo et al., 2013; Jiang et al., 2016) are
 566 isotopically comparable to our rocks in the Palaeoproterozoic. Although the same trends are observed in
 567 younger orogenies, the resemblance cannot be associated to Archaean tectonics because the magmatism
 568 related is drastically different. The huge majority of magmas formed in the Phanerozoic contrast greatly
 569 with the TTGs presented in this study because they belong to the BADR series (see Figure 1).

570

571

6 – The Global Transition to Plate Tectonics

572 TTG and/or sanukitoid magmas have now been recorded from the
573 Palaeoarchaean to Neoproterozoic in almost all cratons worldwide and in most cases with
574 a clear evolutionary trend from TTG to sanukitoid (e.g. [Laurent et al., 2014](#); [Halla et al.,](#)
575 [2017](#)). The timespan over which this evolution occurred is generally considered to be in
576 the Archaean (e.g. [Nebel et al., 2018](#)). TTG generation mostly involved melting of basaltic
577 sources after their production in the upper mantle ([Moyen and Laurent, 2018](#)). It has
578 been suggested that a system governed by stacking of oceanic slabs ([Hastie et al., 2016](#)),
579 subsequently led to eclogitization and steepening of the downthrust/proto-subduction
580 angle to open the mantle wedge ([Bédard et al., 2018](#)). Subsequent interaction with
581 volatiles, sediments and TTG-like melts from the downgoing slab(s) enriched the mantle
582 wedge and generated sanukitoid magmas in the igneous record for the first time at c. 3.0
583 Ga ([Laurent et al., 2011; 2014](#)). The system marks the growth of the depleted mantle and
584 the continental crust and must, therefore, be connected with the generation of the
585 subcontinental lithospheric mantle (SCLM) ([Fowler & Rollinson, 2012](#)). When the upper
586 mantle became mostly depleted, this system slowed to a halt ([Moyen and Laurent,](#)
587 [2018](#)), which coincides with the proposed magmatic lull ([Spencer et al., 2018](#)).

588 The TTG-sanukitoid transition, therefore, marks not only a geochemical
589 evolution, but also a tectonic context of continent-driven imbrication of oceanic slabs
590 ([Bédard, 2018](#)). This secular evolution is not unequivocally a mark of a modern-style of
591 subduction-driven plate tectonics for two reasons: 1) the higher mantle temperature (c.
592 250 °C above present day, [Condie et al., 2016](#)) and the relatively weaker and more
593 buoyant oceanic crust do not allow the generation of tensional stress after slab pull
594 transmission; consequently, 2) downwelling forces are not efficient in dragging down

595 cold slabs to higher pressures and generating the low dT/dP rocks, which comprise a
596 hallmark of the subduction-driven plate world (Stern, 2018). The transition, rather,
597 represents a gestational period of a repeated failure of the start of subduction in plate
598 tectonics (Cawood et al., 2018; Nebel et al., 2018), consumption of the undepleted
599 mantle, generation of the SCLM and continental crust growth (Moyen and Laurent, 2018;
600 Bédard, 2018; Dhuime et al., 2018).

601 The new data presented here from the Mineiro belt demonstrate that similarities
602 between Archaean and Palaeoproterozoic TTG-sanukitoid suites are not only recorded
603 by the bulk geochemistry (Moreira et al, 2018), but also by the isotopic systems, which
604 show closely similar evolutionary patterns. In Figure 8, for example, Hf isotope data
605 compiled from Archaean TTG-sanukitoid sequences (and associated hybrid magmas) are
606 undeniably analogous to the linear evolution presented by the samples of this study:
607 TTGs were derived from short-lived basaltic sources; they evolved towards
608 subchondritic values and were replaced by sanukitoid magmatism during a timeframe of
609 roughly 200 Myr. This pattern happens, diachronously, in almost all cratons worldwide
610 and is also observed in the Sm-Nd isotopic system, interpreted as incremental
611 reworking and recycling of the crust (Laurent et al., 2014). Supramantle $\delta^{18}\text{O}$ values are
612 similar to the range of other sanukitoid magmas worldwide (Fig. 5), suggesting a similar
613 influence of sediments within the nascent mantle wedge. At the other extreme,
614 comparable low $\delta^{18}\text{O}$ values (as low as +4.0‰) have been ascribed to high-temperature
615 altered gabbroic sources of the TTG rocks dating back to 3.8 Ga (Fig. 5). In short, there is
616 no fundamental difference in petrogenetic process in the TTG-sanukitoid transition from
617 Neoarchaean to Palaeoproterozoic examples.

618 It is also evident that deep penetration of oceanic lithosphere into the mantle is
619 required to generate the mantle wedge. Thus, sanukitoids can be rationalised by slab
620 break-off after attempted subduction of buoyant continental lithosphere (Halla et al.,
621 2009), which implies a collisional setting controlled by lateral drift of rigid plates and
622 presence of a mantle wedge. Importantly, it also clearly demonstrates that mantle wedge
623 interaction does not prove modern-style subduction. However, at c. 2.0 Ga, following the
624 assemblage of the Columbia/Nuna supercontinent, cold and steep subduction had
625 established a new plate tectonic style (e.g. Brown and Johnson, 2018). This may have
626 been irreversibly triggered by the supercontinent cycle after insulation and
627 reorganization of the mantle (Spencer et al., 2018). Therefore, we propose that this final
628 TTG-sanukitoid transition is the last gasp of an ante-plate tectonics regime, marked by
629 multiple, sequential, stalled attempts to initiate the modern-style of subduction on
630 Earth.

631 **7 – Conclusions**

632 The occurrence of a narrow evolution window from TTG to sanukitoid and
633 related magmas in the Mineiro Belt during the ‘global magmatic lull’ provides
634 indisputable evidence for crustal growth, reworking and recycling during the early
635 Palaeoproterozoic.

636 This TTG-sanukitoid transition involves proto-subduction-driven plate tectonics,
637 here termed as ante-plate tectonics, and it is petrogenetically similar to the Neoarchean
638 evolution of granitoid rocks reported worldwide.

639 The 2.35 Ga TTG derives from a short-lived high-temperature hydrothermally
640 altered metabasaltic source; the interaction of similar TTG-like melts, within the mantle

641 wedge, and subducted sediments marks the generation of sanukitoids some 200 Myr
642 later.

643 The opening of the mantle wedge began at c. 2.2 Ga, during proto-subduction
644 initiation. Seventy million years elapsed between the opening of the mantle wedge and
645 production of sediment-contaminated magmas, in the form of sanukitoid, high Ba-Sr and
646 hybrid granitoid suites at c. 2.13 Ga.

647 The opening of the mantle wedge also triggered the melting of Archaean basaltic
648 source and generation of 2.18 – 2.2 Ga tonalitic magmas.

649 This latest TTG-sanukitoid transition represents the last vestige of an ante-plate
650 tectonics regime initiated during the Palaeoproterozoic magmatic lull. After this tipping
651 point, the Earth was inescapably locked into the modern plate tectonic regime.

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663 **References**

- 664 Ávila, C.A., Teixeira, W., Bongiolo, E.M., Dussin, I.A. and Vieira, T.A.T., 2014. Rhyacian evolution of
665 subvolcanic and metasedimentary rocks of the southern segment of the Mineiro belt, São
666 Francisco Craton, Brazil. *Precambrian Research*, 243, pp.221-251.
- 667 Beall, A.P., Moresi, L. and Cooper, C.M., 2018. Formation of cratonic lithosphere during the
668 initiation of plate tectonics. *Geology*, 46(6), pp.487-490.
- 669 Bédard, J.H., 2018. Stagnant lids and mantle overturns: implications for Archaean tectonics,
670 magmagenesis, crustal growth, mantle evolution, and the start of plate tectonics. *Geoscience*
671 *Frontiers* 9, 19-49.

- 672 Brown, M. and Johnson, T., 2018. Secular change in metamorphism and the onset of global plate
673 tectonics. *American Mineralogist*, 103(2), pp.181-196.
- 674 Cawood, P.A., Hawkesworth, C.J. and Dhuime, B., 2012. Detrital zircon record and tectonic
675 setting. *Geology*, 40(10), pp.875-878.
- 676 Cawood, P.A., Hawkesworth, C.J., Pisarevsky, S.A., Dhuime, B., Capitanio, F.A. and Nebel, O., 2018.
677 Geological archive of the onset of plate tectonics. *Philosophical Transactions of the Royal Society*
678 *A: Mathematical, Physical and Engineering Sciences*, 376(2132), p.20170405.
- 679 Condie, K.C., Aster, R.C. and Van Hunen, J., 2016. A great thermal divergence in the mantle
680 beginning 2.5 Ga: Geochemical constraints from greenstone basalts and komatiites. *Geoscience*
681 *Frontiers*, 7(4), pp.543-553.
- 682 Dhuime, B., Hawkesworth, C.J., Delavault, H. and Cawood, P.A., 2018. Rates of generation and
683 destruction of the continental crust: implications for continental growth. *Philosophical*
684 *Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*,
685 376(2132), p.20170403.
- 686 Eiler, J.M., 2001. Oxygen isotope variations of basaltic lavas and upper mantle rocks: Reviews in
687 *Mineralogy and Geochemistry*, v. 43, p. 319–364, doi: 10.2138 /gsrmg .43 .1 .319.
- 688 Foley, S.F., Buhre, S. and Jacob, D.E., 2003. Evolution of the Archaean crust by delamination and
689 shallow subduction. *Nature*, 421(6920), p.249.
- 690 Fowler, M.B., Kocks, H., Darbyshire, D.P.F. and Greenwood, P.B., 2008. Petrogenesis of high Ba–Sr
691 plutons from the northern highlands Terrane of the British Caledonian Province. *Lithos*, 105(1-
692 2), pp.129-148.
- 693 Fowler, M., Rollinson, H., 2012. Phanerozoic sanukitoids from Caledonian Scotland: implications
694 for Archean subduction. *Geology*, 40(12), pp.1079-1082.
- 695 Gregory, R.T. and Taylor Jr, H.P., 1981. An oxygen isotope profile in a section of Cretaceous
696 oceanic crust, Samail Ophiolite, Oman: Evidence for $\delta^{18}\text{O}$ buffering of the oceans by deep (> 5
697 km) seawater-hydrothermal circulation at mid-ocean ridges. *Journal of Geophysical Research:*
698 *Solid Earth*, 86(B4), pp.2737-2755.
- 699 Halla, J., van Hunen, J., Heilimo, E. and Hölttä, P., 2009. Geochemical and numerical constraints on
700 Neoproterozoic plate tectonics. *Precambrian Research*, 174(1-2), pp.155-162.
- 701 Halla, J., Whitehouse, M.J., Ahmad, T. and Bagai, Z., 2017. Archaean granitoids: an overview and
702 significance from a tectonic perspective. *Geological Society, London, Special Publications*,
703 449(1), pp.1-18.
- 704 Hastie, A.R., Fitton, J.G., Bromiley, G.D., Butler, I.B. and Odling, N.W., 2016. The origin of Earth's
705 first continents and the onset of plate tectonics. *Geology*, 44(10), pp.855-858.
- 706 Hawkesworth, C.J. and Kemp, A.I.S., 2006. Using hafnium and oxygen isotopes in zircons to
707 unravel the record of crustal evolution. *Chemical Geology*, 226(3-4), pp.144-162.
- 708 Heilbron, M., Cordani, U.G., Alkmim, F.F. and Reis, H.L., 2017. Tectonic genealogy of a miniature
709 continent. In *São Francisco Craton, Eastern Brazil* (pp. 321-331). Springer, Cham.
- 710 Heilimo, E., Halla, J., Andersen, T. and Huhma, H., 2013. Neoproterozoic crustal recycling and mantle
711 metasomatism: Hf–Nd–Pb–O isotope evidence from sanukitoids of the Fennoscandian shield.
712 *Precambrian Research*, 228, pp.250-266.

- 713 Heilimo, E., Halla, J. and Hölttä, P., 2010. Discrimination and origin of the sanukitoid series:
714 geochemical constraints from the Neoproterozoic western Karelian Province (Finland). *Lithos*,
715 115(1-4), pp.27-39.
- 716 Heilimo, E., Halla, J. and Huhma, H., 2011. Single-grain zircon U–Pb age constraints of the
717 western and eastern sanukitoid zones in the Finnish part of the Karelian Province. *Lithos*, 121(1-
718 4), pp.87-99.
- 719 Hiess, J., Bennett, V.C., Nutman, A.P. and Williams, I.S., 2009. In situ U–Pb, O and Hf isotopic
720 compositions of zircon and olivine from Eoarchaeoan rocks, West Greenland: new insights to
721 making old crust. *Geochimica et Cosmochimica Acta*, 73(15), pp.4489-4516.
- 722 Hopkinson, T.N., Harris, N.B., Warren, C.J., Spencer, C.J., Roberts, N.M., Horstwood, M.S. and
723 Parrish, R.R., 2017. The identification and significance of pure sediment-derived granites. *Earth
724 and Planetary Science Letters*, 467, pp.57-63.
- 725 Jiang, N., Guo, J., Fan, W., Hu, J., Zong, K. and Zhang, S., 2016. Archean TTGs and sanukitoids from
726 the Jiaobei terrain, North China craton: Insights into crustal growth and mantle metasomatism.
727 *Precambrian Research*, 281, pp.656-672.
- 728 Kemp, A.I.S., Hawkesworth, C.J., Paterson, B.A. and Kinny, P.D., 2006. Episodic growth of the
729 Gondwana supercontinent from hafnium and oxygen isotopes in zircon. *Nature*, 439(7076),
730 pp.580-583.
- 731 Laurent, O., Björnson, J., Wotzlaw, J.F., Bretscher, S., Silva, M.P., Moyen, J.F., Ulmer, P. and
732 Bachmann, O., 2020. Earth's earliest granitoids are crystal-rich magma reservoirs tapped by
733 silicic eruptions. *Nature Geoscience*, pp.1-7.
- 734 Laurent, O., Martin, H., Doucelance, R., Moyen, J.F. and Paquette, J.L., 2011. Geochemistry and
735 petrogenesis of high-K "sanukitoids" from the Bulai pluton, Central Limpopo Belt, South Africa:
736 Implications for geodynamic changes at the Archaean–Proterozoic boundary. *Lithos*, 123(1-4),
737 pp.73-91.
- 738 Laurent, O., Martin, H., Moyen, J.F. and Doucelance, R., 2014. The diversity and evolution of late-
739 Archean granitoids: Evidence for the onset of "modern-style" plate tectonics between 3.0 and 2.5
740 Ga. *Lithos*, 205, pp.208-235.
- 741 Martin, H., Moyen, J.F. and Rapp, R., 2009. The sanukitoid series: magmatism at the Archaean–
742 Proterozoic transition. *Earth and Environmental Science Transactions of the Royal Society of
743 Edinburgh*, 100(1-2), pp.15-33.
- 744 Martínez Dopico, C.I., Lana, C., Moreira, H.S., Cassino, L.F. and Alkmim, F.F., 2017. U–Pb ages and
745 Hf-isotope data of detrital zircons from the late Neoproterozoic–Paleoproterozoic Minas Basin, SE
746 Brazil. *Precambrian Research*, 291, pp.143-161.
- 747 Mikkola, P., Huhma, H., Heilimo, E. and Whitehouse, M., 2011. Archean crustal evolution of the
748 Suomussalmi district as part of the Kianta Complex, Karelia: constraints from geochemistry and
749 isotopes of granitoids. *Lithos*, 125(1-2), pp.287-307.
- 750 Moreira, H., Seixas, L., Storey, C., Fowler, M., Lasalle, S., Stevenson, R. and Lana, C., 2018.
751 Evolution of siderian juvenile crust to rhyacian high Ba–Sr magmatism in the Mineiro Belt,
752 southern São Francisco Craton. *Geoscience Frontiers*, 9(4), pp.977-995.
- 753 Moyen, J.F. and Martin, H., 2012. Forty years of TTG research. *Lithos*, 148, pp.312-336.

- 754 Moyen, J.F. and Laurent, O., 2018. Archaean tectonic systems: a view from igneous rocks. *Lithos*,
755 302, pp.99-125.
- 756 Nebel, O., Capitanio, F.A., Moyen, J.F., Weinberg, R.F., Clos, F., Nebel-Jacobsen, Y.J. and Cawood,
757 P.A., 2018. When crust comes of age: on the chemical evolution of Archaean, felsic continental
758 crust by crustal drip tectonics. *Philosophical Transactions of the Royal Society A: Mathematical,*
759 *Physical and Engineering Sciences*, 376(2132), p.20180103.
- 760 Payne, J.L., McInerney, D.J., Barovich, K.M., Kirkland, C.L., Pearson, N.J. and Hand, M., 2016.
761 Strengths and limitations of zircon Lu-Hf and O isotopes in modelling crustal growth. *Lithos*,
762 248, pp.175-192.
- 763 Seixas, L.A.R., Bardintzeff, J.M., Stevenson, R. and Bonin, B., 2013. Petrology of the high-Mg
764 tonalites and dioritic enclaves of the ca. 2130 Ma Alto Maranhão suite: Evidence for a major
765 juvenile crustal addition event during the Rhyacian orogenesis, Mineiro Belt, southeast Brazil.
766 *Precambrian Research*, 238, pp.18-41.
- 767 Seixas, L.A.R., David, J. and Stevenson, R., 2012. Geochemistry, Nd isotopes and U-Pb
768 geochronology of a 2350 Ma TTG suite, Minas Gerais, Brazil: implications for the crustal
769 evolution of the southern São Francisco craton. *Precambrian Research*, 196, pp.61-80.
- 770 Shieh, Y.N. and Schwarcz, H.P., 1978. The oxygen isotope composition of the surface crystalline
771 rocks of the Canadian Shield. *Canadian Journal of Earth Sciences*, 15(11), pp.1773-1782.
- 772 Shirey, S.B., Hanson, G.N., 1984. Mantle derived Archaean monzodiorites and trachyandesites.
773 *Nature*. 310, 222-224.
- 774 Smithies, R.H., 2000. The Archaean tonalite-trondhjemite-granodiorite (TTG) series is not an
775 analogue of Cenozoic adakite. *Earth and Planetary Science Letters*, 182(1), pp.115-125.
- 776 Spencer, C.J., Murphy, J.B., Kirkland, C.L., Liu, Y. and Mitchell, R.N., 2018. A Palaeoproterozoic
777 tectono-magmatic lull as a potential trigger for the supercontinent cycle. *Nature Geoscience*, p.1.
- 778 Stern, R.J., 2018. The evolution of plate tectonics. *Philosophical Transactions of the Royal Society*
779 *A: Mathematical, Physical and Engineering Sciences*, 376(2132), p.20170406.
- 780 Stille, P., Unruh, D.M. and Tatsumoto, M., 1986. Pb, Sr, Nd, and Hf isotopic constraints on the
781 origin of Hawaiian basalts and evidence for a unique mantle source. *Geochimica et*
782 *Cosmochimica Acta*, 50(10), pp.2303-2319.
- 783 Teixeira, W., Ávila, C.A., Dussin, I.A., Neto, A.C., Bongioiolo, E.M., Santos, J.O. and Barbosa, N.S., 2015.
784 A juvenile accretion episode (2.35-2.32 Ga) in the Mineiro belt and its role to the Minas
785 accretionary orogeny: Zircon U-Pb-Hf and geochemical evidences. *Precambrian Research*, 256,
786 pp.148-169.
- 787 Valley, J.W., 2003. Oxygen isotopes in zircon. *Reviews in mineralogy and geochemistry*, 53(1),
788 pp.343-385.
- 789 Vervoort, J.D., Patchett, P.J., Blichert-Toft, J. and Albarède, F., 1999. Relationships between Lu-Hf
790 and Sm-Nd isotopic systems in the global sedimentary system. *Earth and Planetary Science*
791 *Letters*, 168(1), pp.79-99.
- 792 Workman, R.K. and Hart, S.R., 2005. Major and trace element composition of the depleted MORB
793 mantle (DMM). *Earth and Planetary Science Letters*, 231(1-2), pp.53-72.

- 794 Zeh, A., Gerdes, A. and Barton Jr, J.M., 2009. Archean accretion and crustal evolution of the
795 Kalahari Craton—the zircon age and Hf isotope record of granitic rocks from
796 Barberton/Swaziland to the Francistown Arc. *Journal of Petrology*, 50(5), pp.933-966.
- 797 Zeh, A., Jaguin, J., Poujol, M., Boulvais, P., Block, S. and Paquette, J.L., 2013. Juvenile crust
798 formation in the northeastern Kaapvaal Craton at 2.97 Ga—Implications for Archean terrane
799 accretion, and the source of the Pietersburg gold. *Precambrian Research*, 233, pp.20-43.
- 800 Zhao, Z.F., Zheng, Y.F., 2003. Calculation of oxygen isotope fractionation in magmatic rocks.
801 *Chemical Geology*, 193(1-2), pp.59-80.