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Earth's evolving geodynamic regime recorded by titanium isotopes

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Abstract

Earth's mantle has a two-layered structure, with the upper and lower mantle domains separated by a seismic discontinuity at ~660 km^{1,2}. The extent of mass transfer between these mantle domains throughout Earth's history is, however, poorly understood.

24 **Continental crust extraction results in Ti stable isotopic fractionation, producing**
25 **isotopically-light melting residues³⁻⁷. Mantle recycling of these components can impart Ti**
26 **isotope variability that is trackable in deep time. We report ultra-high precision ⁴⁹Ti/⁴⁷Ti**
27 **ratios for chondrites, ancient terrestrial mantle-derived lavas ranging from 3.8 to 2.0 Ga**
28 **and modern oceanic island basalts (OIBs). Our new Ti bulk silicate Earth (BSE) estimate**
29 **based on chondrites is 0.052±0.006‰ heavier than the modern upper mantle sampled by**
30 **normal-type mid-ocean ridge basalts (N-MORBs). The ⁴⁹Ti/⁴⁷Ti ratio of Earth's upper**
31 **mantle was chondritic before 3.5 Ga and evolved to a N-MORB-like composition between**
32 **~3.5-2.7 Ga, establishing that more continental crust was extracted during this epoch.**
33 **The +0.052±0.006‰ offset between BSE and N-MORBs requires that <30% of Earth's**
34 **mantle equilibrated with recycled crustal material, implying limited mass exchange**
35 **between the upper and lower mantle and, therefore, preservation of a primordial lower**
36 **mantle reservoir for most of Earth's geologic history. Modern OIBs record variable**
37 **⁴⁹Ti/⁴⁷Ti ratios ranging from chondritic to N-MORBs compositions, indicating ongoing**
38 **disruption of Earth's primordial mantle. Thus, modern-style plate tectonics with high**
39 **mass transfer between the upper and lower mantle only represents a recent feature of**
40 **Earth's history.**

41 **Main**

42 The accretion history of terrestrial planets is punctuated by a global magma ocean stage, which
43 leads to planetary differentiation and the establishment of major reservoirs such as core, mantle,
44 and crust. The subsequent evolution and modification of these reservoirs can significantly
45 impact the planets' thermal and geodynamic regime. Based on mineralogy, rheology, and
46 seismic velocity, it has been established that the structure of Earth's mantle is layered with a
47 major seismic discontinuity at ~660 km separating the upper and lower mantle domains^{1,2}.
48 However, the extent to which mass transfer occurs within the mantle throughout the geologic

49 history remains highly debated. Seismic tomography data suggest that subducted slabs can
50 penetrate into the lower mantle, and at the current rate of mass exchange, Earth's primordial
51 mantle **is not predicted to survive** after prolonged whole mantle-scale convection⁸⁻¹⁰.
52 Meanwhile, studies based on noble gases¹¹⁻¹⁵ as well as tungsten¹⁶ and neodymium¹⁷ isotopes,
53 have suggested instead the existence of primordial mantle domains in the modern deep Earth.
54 Although the preservation of a primordial lower mantle reservoir over long geological
55 timescales is debated^{18,19}, some geodynamics models show that that preservation of primordial
56 mantle domains can occur in a modern-style, whole mantle convection regime characterized
57 by deep subduction²⁰. In addition, both numerical modelling and geological observations²¹⁻²⁵
58 suggest that Earth's convection regime and, hence, the style of slab subduction may have also
59 evolved significantly through time as a consequence of change in the heat flux and heat
60 transfer^{25,26}. As such, a potential solution to the conundrum is that the high mass transfer
61 between the upper and lower mantle inferred from seismic tomography is a relatively recent
62 feature of Earth's geologic history such that the primordial, less-degassed lower mantle
63 reservoir has been undergoing disruption but is not fully destroyed yet²⁷. This hypothesis has
64 not been fully evaluated given the lack of an unambiguous geochemical tool that can faithfully
65 trace mass exchange between mantle and crustal reservoirs in deep time.

66 The stable isotope geochemistry of the refractory lithophile element Ti is a novel tracer that
67 can potentially provide a historical record of mass exchange processes between mantle and
68 crustal reservoirs. The continental crust of Earth can be formed through either partial melting
69 of subducting slabs²⁸ and/or thickened mafic crust^{29,30}, which produces felsic melts. Such
70 magmatic processes can result in significant Ti isotopic fractionation between the felsic silicate
71 melts and the residue from this melt extraction, i.e. melting residues³⁻⁷. In contrast, partial
72 melting of mantle peridotites seemingly does not fractionate Ti isotopes^{3,4}. In detail, the $\delta^{49}\text{Ti}$
73 values (i.e., the per mil deviation of the $^{49}\text{Ti}/^{47}\text{Ti}$ ratio relative to the OL-Ti standard) of

74 Archean tonalite-trondhjemite-granodiorite (TTG) rocks and Phanerozoic granites^{5,7}, as well
75 as those of evolved volcanic rocks^{3,6,7,31,32} can be up to +2.0‰ higher than that of oxide-
76 undersaturated mafic/ultramafic rocks^{3,4}. Thus, recycling of melting residues from extraction
77 of continental crust via either delamination or subduction is predicted to generate mantle
78 reservoirs with heterogeneous $\delta^{49}\text{Ti}$ (ref. 4). Additionally, the largely immobile nature of Ti
79 allows for a thorough investigation of Ti stable isotope composition of Archean mantle-derived
80 rocks despite alteration and metamorphism. However, the application of stable Ti isotopes to
81 understand mantle-crust differentiation and crustal recycling processes is hampered by the
82 scatter in the $\delta^{49}\text{Ti}$ values of chondrite meteorites used to define the bulk silicate Earth (BSE)
83 reference value³³⁻³⁵, which is likely due to a combination of factors such as sample
84 heterogeneity, analytical biases and uncertainties as well as imperfect correction for mass-
85 independent nucleosynthetic effects on ^{46}Ti (see **Methods**).

86

87 **The $\delta^{49}\text{Ti}$ value of Bulk Silicate Earth**

88 We developed novel analytical methods for **ultra**-high precision Ti isotope measurements using
89 the next generation of multi-collector inductively coupled plasma source mass spectrometers
90 (the Neoma MC-ICP-MS). Our protocol allows for the concomitant determination of the mass-
91 independent (± 0.15 epsilon on the mass bias corrected $^{50}\text{Ti}/^{47}\text{Ti}$ ratio) and mass-dependent Ti
92 stable isotope composition (± 0.010 ‰ for $\delta^{49}\text{Ti}$) of individual samples to **ultra**-high precision
93 (see details in **Methods**). Using this approach, we analysed 24 chondrite meteorites covering
94 all major chondrite classes. Despite significant variability in $\epsilon^{50}\text{Ti}$ values (i.e., the per ten
95 thousand deviation of the mass bias corrected $^{50}\text{Ti}/^{47}\text{Ti}$ ratio relative to the OL-Ti standard)
96 between the analysed chondrites, they return a restricted range of $\delta^{49}\text{Ti}$ values that define a
97 weighed mean of $+0.053 \pm 0.005$ ‰ (2SE, $n = 22$), excluding one CV3 [NWA2364] and one

98 LL3 [Talbachat n'aït Isfoul] that are likely subject to sample heterogeneity (see **Methods**),
99 which represents a threefold improvement in precision relative to previous estimates³³⁻³⁵. The
100 first important observation emerging from the new BSE estimate is that it is distinct from the
101 composition of the modern depleted mantle as sampled by normal-type mid-ocean ridge
102 basalts^{3,4} (N-MORBs) ($\delta^{49}\text{Ti} = +0.001 \pm 0.004\%$, 2SE, $n = 12$) that are thought to represent
103 the 'depleted MORB mantle'.

104

105 **Earth's mantle $\delta^{49}\text{Ti}$ value in deep time**

106 **To** better understand the significance of the lighter, non-chondritic Ti isotope composition of
107 Earth's modern depleted MORB mantle reservoirs, we analysed a set of terrestrial samples
108 including 31 well-characterised Archean to Proterozoic samples (one tonalitic and 30 mafic to
109 ultramafic) with crystallization ages ranging from ~ 3.8 to ~ 2.0 Ga and 21 modern OIBs that
110 have not experienced Fe-Ti oxide fractionation. The Archean to Proterozoic samples include
111 amphibolites (~ 3.8 Ga), one Amitsoq gneiss (3.8-3.7 Ga), **Ameralik** dykes (~ 3.4 Ga) and
112 Kangâmiut dykes (~ 2.0 Ga) **from Southwest** Greenland as well as peridotitic to basaltic
113 komatiites and tholeiitic basalts from the **Kaapvaal Craton** (~ 3.48 Ga Komati Formation and
114 ~ 3.33 Ga Kromberg Formation) and Munro Township from the Abitibi Greenstone belt (~ 2.7
115 Ga). The modern OIBs are from the Iceland, Caroline, and Samoa hotspots, which have Sr and
116 Nd isotope compositions spanning along the curve defined by the depleted MORB mantle
117 (DMM), the prevalent mantle (PREMA) and the enriched mantle type II (EM-II) (Extended
118 Data Fig. 1a). As shown in Fig. 1, the early Archean mantle-derived rocks have $\delta^{49}\text{Ti}$ values
119 indistinguishable from bulk chondrites, whereas the middle to late Archean samples have
120 progressively lighter compositions that extend towards the $\delta^{49}\text{Ti}$ values of modern N-MORBs.
121 In contrast, the ~ 2.0 Ga Kangâmiut dykes and modern OIB samples have highly variable $\delta^{49}\text{Ti}$

122 values that range from the chondritic composition to values well below that of modern N-
123 MORBs (Fig. 1). One ~3.8 Ga tonalitic sample (SD-2) from Isua records a high $\delta^{49}\text{Ti}$ value of
124 $+0.205 \pm 0.003\text{‰}$, which is indistinguishable from previously reported $\delta^{49}\text{Ti}$ values for
125 tonalite-trondhjemite-granodiorite (TTG) rocks from the Kaapvaal Craton and Acasta gneiss
126 complex ($\delta^{49}\text{Ti} = +0.173 \pm 0.030\text{‰}$ to $+0.570 \pm 0.030\text{‰}$)^{5,7} (Fig. 1).

127 Our high precision $\delta^{49}\text{Ti}$ data for early Archean komatiitic to basaltic rocks allows us to
128 evaluate an earlier inference that partial melting of mantle peridotites on Earth produces only
129 minor mass-dependent Ti isotopic fractionation^{3,4}. Komatiitic magmas formed by ~25-40%
130 partial melting of their mantle source^{36,37} and, as such, are expected to have extracted > 90%
131 Ti from their sources. In contrast, basaltic magmas that form from lower degrees of mantle
132 partial melting (~5-10%, e.g., the ~3.8 Ga Isua pillow-textured metabasalts or ~3.48 Ga
133 [Barberton](#) basaltic komatiites) extract approximately half of the Ti from their sources. Thus, a
134 resolvable difference in $\delta^{49}\text{Ti}$ is expected between the two types of magmas if there is
135 significant Ti isotopic fractionation between silicate melts and melting residues during partial
136 melting of mantle peridotites. However, the comparable $\delta^{49}\text{Ti}$ values between the ~3.8 Ga Isua
137 metabasalts ($+0.048 \pm 0.005\text{‰}$, 2SE, n = 5), the ~3.48 Ga Barberton komatiites ($+0.044 \pm$
138 0.009‰ , 2SE, n = 4) to basaltic komatiites ($+0.048 \pm 0.008\text{‰}$, 2SE, n = 4) and chondrite
139 meteorites ($+0.053 \pm 0.005\text{‰}$, 2SE, n = 22) suggests that, in agreement with previous
140 inferences based on various lines of evidence^{3,4,38,39}, Ti isotopic fractionation between melts
141 and residues from mantle partial melting is negligible. Thus, the near-zero $\Delta^{49}\text{Ti}_{\text{melt-residue}}$
142 values inferred here suggest that metal-saturated melting with presence of Ti^{3+} is not relevant
143 to the generation of terrestrial mafic/ultramafic magmas⁴⁰. Moreover, the limited fractionation
144 of Ti from mantle partial melting on Earth implied by our results supports the hypothesis that
145 the studied mantle-derived rocks faithfully record the $\delta^{49}\text{Ti}$ composition of their mantle sources.
146 As such, our data suggest that sources of the studied mantle-derived rocks were characterised

147 by chondritic $\delta^{49}\text{Ti}$ values ($\delta^{49}\text{Ti} = +0.053 \pm 0.005\%$) around $\sim 3.8\text{-}3.5$ Ga and evolved towards
148 a modern depleted MORB mantle composition ($\delta^{49}\text{Ti} = +0.001 \pm 0.005\%$) by ~ 2.7 Ga. This
149 secular evolution is observed in both [Southwest Greenland and the Kaapvaal Craton](#) and in line
150 with the lower $\delta^{49}\text{Ti}$ values observed in the late Archean mantle-derived rocks from Belingwe,
151 Yilgarn and Abitibi. In comparison, the ~ 2.0 Ga Kangâmiut dykes and modern OIBs were
152 derived from the mantle sources different from the modern depleted MORB mantle reservoir.

153

154 [A long-lived primordial lower mantle](#)

155 As indicated by the heavy Ti isotopic composition of Archean TTGs, Phanerozoic granites and
156 differentiated volcanic rocks^{3,5,6,7,31,32}, the formation of a felsic continental crust results in the
157 production of an isotopically light crustal melting residue. Thus, we interpret the observed
158 secular change in the Ti isotopic composition of the Archean mantle as evidence for the
159 progressive recycling of melting residues via delamination or subduction to Earth's mantle
160 following continental crust extraction^{41,42}, requiring full isotopic equilibration between the
161 mantle reservoir and the admixed melting residues. Notably, the observed shift towards lower
162 $\delta^{49}\text{Ti}$ values in the source of Archean mantle-derived rocks between ~ 3.5 and ~ 2.7 Ga coincides
163 with the major epoch of continental crust extraction proposed in earlier studies^{43,44} (Fig. 2).
164 Adopting the current mass of continental crust (i.e., $\sim 0.55\%$ of [the BSE](#)), neither whole mantle
165 [convection nor](#) layered mantle convection with limited mass transfer between the upper and
166 lower [mantle can](#) reproduce the $\sim 0.052\%$ fractionation in the mantle by recycling of melting
167 residues from continental crust formation (Fig. 2). However, it is possible to generate the $\delta^{49}\text{Ti}$
168 effect of $\sim 0.052\%$ via layered mantle convection with limited mass transfer between the upper
169 and lower mantle only if the mass of continental crust produced over geological time is greater
170 than the current mass, namely $\sim 1.43\%$ of [the BSE](#). Such a high production of continental crust

171 throughout Earth's history has also been inferred in the recent continental crust growth
172 models⁴⁵, based on the integration of various proxies such as neodymium and hafnium isotopes.
173 This consistency between studies using distinct geochemical tracers suggests that the mass of
174 continental crust produced in Earth's history likely exceeded its present-day value, and a large
175 portion of this crust has been destroyed and recycled into the mantle, meaning that a high mass
176 of ancient continental crust has been stored in the deep mantle. An important finding of this
177 work is that only a small fraction of Earth's mantle (e.g., ~20%) has equilibrated with melting
178 residues from continental crust extraction, implying limited mass transfer between the upper
179 and lower mantle in the Archean. Irrespective of an apparent separation of lower and upper
180 mantle, after the Archean, some upwelling of primordial material from the lower mantle likely
181 has occurred since 2 billion years ago as evidenced by the elevated $\delta^{49}\text{Ti}$ values in some of the
182 studied ~2.0 Ga Kangâmiut dykes and modern OIBs (Fig. 2).

183 Modern OIBs, which are thought to sample a deeper mantle reservoir than MORBs⁴⁶, provide
184 an opportunity to explore the possible survival of a primordial material in the lower mantle.
185 Although the sources of modern OIBs and enriched-MORBs (E-MORBs) record large $\delta^{49}\text{Ti}$
186 variability, most have $\delta^{49}\text{Ti}$ values that are 0.030-0.045‰ heavier than the composition of the
187 modern depleted MORB mantle sampled by N-MORBs (Fig. 3). Given that marine sediments
188 since the Archean constantly record high $\delta^{49}\text{Ti}$ values (+0.20‰ on average^{5,6}), it is possible
189 that the elevated $\delta^{49}\text{Ti}$ signature of the OIB sources is a result of admixing of subducted marine
190 sediments or, alternatively, upper continental crust material into a modern depleted MORB
191 mantle reservoir. However, increasing the $\delta^{49}\text{Ti}$ value of a hybrid mantle source by 0.030-0.045‰
192 via this process should also lead to highly radiogenic Sr isotopic signatures from sediments or
193 upper continental crust⁴⁷ in the OIB lavas, which is not observed here, except for some lavas
194 from the Samoan hotspot showing $^{87}\text{Sr}/^{86}\text{Sr}$ ratios extending toward EM-II (Extended Data Fig.
195 1a). Thus, the predominantly heavy $\delta^{49}\text{Ti}$ values of modern OIBs requires sampling of a mantle

196 source that did not equilibrate with recycled crustal melting residues, which we infer to
197 represent a primordial **lower** mantle reservoir underlying the modern depleted MORB mantle
198 (Fig. 3). Nonetheless, $\delta^{49}\text{Ti}$ heterogeneity exists within the mantle sources of OIBs. The lower
199 $\delta^{49}\text{Ti}$ values relative to the chondritic composition appear to provide evidence for injection of
200 not only recycled sediments or upper continental crust, but also melting residues into the lower
201 primordial mantle reservoir. We note that recycling of ancient restites from protocrust
202 extraction in the sources of some OIBs has been suggested based on tungsten isotopes⁴². This
203 introduction of recycled material to the lower mantle traced by Ti isotopes is consistent with
204 seismic tomography of the Earth that suggests a high rate of mass exchange between the upper
205 and lower mantle in modern times^{8,9} and other geochemical evidence that indicate the presence
206 of ancient subducted oceanic lithosphere in the sources of OIBs^{47, 49-51}. It has also been
207 proposed that the anomalous noble gas and tungsten isotope signals in modern OIBs may
208 reflect interaction with core material as opposed to sampling of a primordial mantle reservoir⁵²⁻
209 ⁵⁴. The refractory and lithophile nature of Ti makes its stable isotope composition impervious
210 to the interaction with core material. Thus, the Ti isotope data reported here coupled with the
211 noble gas and tungsten isotope signals identified in modern OIBs^{11-16,55,56} is most consistent
212 with the survival of a primordial, less-degassed mantle reservoir in the modern deep Earth.

213

214 **The evolving geodynamic regime of Earth**

215 Our new Ti isotope data, which require limited mass exchange between the upper and lower
216 mantle over a significant part of Earth's geologic history, provide new insights into Earth's
217 geodynamic evolution. The chondritic or primordial mantle-like $\delta^{49}\text{Ti}$ value of the ~3.8-3.5 Ga
218 upper mantle indicates limited production of felsic continental crust and recycling of melting
219 residues during the early Archean, pointing to a long residence of the primordial crust on

220 Earth's surface. In contrast, progressive enrichment of light Ti isotopes in mantle-derived rocks
221 between ~3.5 to ~2.7 Ga requires an acceleration in the growth of felsic continental crust and
222 the recycling of melting residues into the mantle. The increased rate of crustal production and
223 recycling suggest Earth's transition into a geodynamic regime that allowed for progressive
224 recycling of crustal materials back into the mantle. This is in line with the progressive
225 homogenisation of ^{142}Nd variations preserved in rocks from the same time period^{57,58}. Felsic
226 continental crust can be generated without plate tectonics via partial melting of hydrated basalts
227 at the base of a thickened crust^{29,30,41,59,60} or, alternatively, associated with a tectonic regime
228 that includes active subduction of surface materials^{28,61,62}. Irrespective, the secular evolution of
229 $\delta^{49}\text{Ti}$ recorded by the Archean mantle-derived lavas is best understood to reflect a transition in
230 Earth geodynamic regime promoting accelerated crustal recycling around 3.5 Ga.

231 The mass of the mantle inferred to have equilibrated with the recycled melting residues (< 30%)
232 to explain the shift in Ti isotope composition in mantle-derived rocks is broadly consistent with
233 that of the mantle located above the seismic discontinuity at ~660 km, suggesting that the phase
234 transition associated with this discontinuity may have impeded mass exchange. Such a mantle
235 separation is distinct from modern style plate tectonics that are characterised by deep plate
236 subduction and penetration of subducted slabs into the lower mantle. This may indicate that
237 unlike the modern style **regime**, the subducted slab may have different fates in deep time, which
238 may experience frequent slab break-off under the temperature, composition and H_2O
239 conditions of the Archean upper mantle^{25,26} or, alternatively, accumulate at the transition zone
240 where density contrast between subducted slab and surrounding mantle reverses dramatically⁶³.
241 Thus, prior to 2.7 Ga, recycling and admixing of subducted slabs into the ambient mantle was
242 limited to the highly convective upper mantle region instead of penetrating through the mantle
243 transition zone. The coexistence of primordial and evolved $\delta^{49}\text{Ti}$ signals in modern OIBs and
244 MORBs, respectively, requires that the transition between a layered and whole-mantle

245 convective regime occurred late in Earth's history. Thus, these results give credence to
246 theoretical models that suggest that modern plate tectonics with deep slab penetration
247 represents a transient phase in the evolution of planet^{23,27}.

248 Finally, whereas the fundamental causes for the acceleration in continental crust growth and
249 crustal recycling between 3.5-2.7 Ga remain unclear, our new $\delta^{49}\text{Ti}$ data require a regime of
250 mantle convection with limited mass transfer between upper and lower mantle for a significant
251 part of Earth's history. A possibility is that this epoch represents the onset of a tectonic regime
252 allowing the subduction of plates or, alternatively, frequent crustal thickening, which in both
253 cases will result in partial melting and extraction of felsic continental crust. Irrespective, our
254 data require that efficient recycling and homogenization of the melting residues from felsic
255 continental crust generation was limited to the upper mantle, which implies the long-term
256 preservation of a primordial lower mantle reservoir. However, the highly variable Ti isotope
257 compositions recorded by modern OIBs suggest that the primordial lower mantle reservoir is
258 undergoing disruption. Thus, modern-style plate tectonics with whole mantle-scale convection
259 and deep penetration of subducted slabs may only represent a transient and recent feature of
260 Earth's history.

261

262 **References**

- 263 1. Kennett, B.L.N. & Engdahl, E.R. Traveltimes for global earthquake location and phase
264 identification. *Geophys. J. Int.* **105**, 429-465 (1991).
- 265 2. Ringwood, A.E. Phase transformations and their bearing on the constitution and dynamics
266 of the mantle. *Geochim. Cosmochim. Acta* **55**, 2083-2110 (1991).
- 267 3. Millet, M.A. et al. Titanium stable isotope investigation of magmatic processes on the Earth
268 and Moon. *Earth Planet. Sci. Lett.* **449**, 197-205 (2016).

- 269 4. Deng, Z., Moynier, F., Sossi, P.A. & Chaussidon, M. Bridging the depleted MORB mantle
270 and the continental crust using titanium isotopes. *Geochem. Perspect. Lett.* **9**, 11-15 (2018).
- 271 5. Greber, N.D. et al. Titanium isotopic evidence for felsic crust and plate tectonics 3.5 billion
272 years ago. *Science* **357**, 1271-1274 (2017).
- 273 6. Deng, Z. et al. Titanium isotopes as a tracer for the plume or island arc affinity of felsic
274 rocks. *Proc. Natl. Acad. Sci. U.S.A.* **116**, 1132-1135 (2019).
- 275 7. Aarons, S.M. et al. Titanium isotopes constrain a magmatic transition at the Hadean-
276 Archean boundary in the Acasta Gneiss Complex. *Sci. Adv.* **6**, eabc9959 (2020) DOI:
277 10.1126/sciadv.abc9959
- 278 8. van der Hilst, R.D., Widiyantoro, S. & Engdahl, E.R. Evidence for deep mantle circulation
279 from global tomography. *Nature* **386**, 578-584 (1997).
- 280 9. Grand, S.P., van der Hilst, R.D. & Widiyantoro, S. High resolution global tomography: a
281 snapshot of convection in the Earth. *GSA Today* **7**, 1-7 (1997).
- 282 10. Fukao, Y. & Obayashi, M. Subducted slabs stagnant above, penetrating through, and
283 trapped below the 660 km discontinuity. *J. Geophys. Res. Solid Earth* **118**, 5920-5938
284 (2013).
- 285 11. Kurz, M.D., Jenkins, W.J. & Hart, S.R. Helium isotopic systematics of oceanic islands and
286 mantle heterogeneity. *Nature* **297**, 43-47 (1982).
- 287 12. Allègre, C.J., Staudacher, T., Sarda, P. & Kurz, M. Constraints on evolution of Earth's
288 mantle from rare gas systematics. *Nature* **303**, 762-766 (1983).
- 289 13. Allègre, C.J., Hofmann, A. & O'Nions, K. The argon constraints on mantle structure.
290 *Geophys. Res. Lett.* **23**, 3555-3557 (1996) .
- 291 14. Mukhopadhyay, S. Early differentiation and volatile accretion recorded in deep-mantle
292 neon and xenon. *Nature* **486**, 101-104 (2012) .

- 293 15. Mukhopadhyay, S. & Parai, R. Noble gases: A record of Earth's evolution and mantle
294 dynamics. *Annu. Rev. Earth Planet. Sci.* **47**, 389-419 (2019) .
- 295 16. Mundl, A. et al. Tungsten-182 heterogeneity in modern ocean island basalts. *Science* **356**,
296 66-69 (2017) .
- 297 17. Peters, B.J., Carlson, R.W., Day, J.M.D. & Horan, M.F. Hadean silicate differentiation
298 preserved by anomalous $^{142}\text{Nd}/^{144}\text{Nd}$ ratios in the Réunion hotspot source. *Nature* **555**, 89-
299 93 (2018) .
- 300 18. Parman, S.W. Helium isotopic evidence for episodic mantle melting and crustal growth.
301 *Nature* **446**, 900-903 (2007).
- 302 19. Albarède, F. Rogue mantle helium and neon. *Science* **319**, 943-945 (2008) .
- 303 20. Kellogg, L.H., Hager, B.H. & van der Hilst, R.D. Compositional stratification in the deep
304 mantle. *Science* **283**, 1881-1884 (1999).
- 305 21. Cawood, P.A. et al. Geological archive of the onset of plate tectonics. *Phil. Trans. R. Soc.*
306 *A* **376**. (2018) DOI: 10.1098/rsta.2017.0405.
- 307 22. Shirey, S.B. & Richardson, S.H. Start of the Wilson Cycle at 3 Ga shown by diamonds
308 from subcontinental mantle. *Science* **333**, 434-436 (2011).
- 309 23. O'Neill, C. et al. A window for plate tectonics in terrestrial planet evolution? *Phys. Earth*
310 *Planet. Inter.* **255**, 80-92 (2016).
- 311 24. Brown, M., Johnson, T. & Gardiner, N.J. Plate tectonics and the Archean Earth. *Annu. Rev.*
312 *Earth Planet. Sci.* **48**, 291-320 (2020).
- 313 25. van Hunen, J. & van den Berg, A.P. Plate tectonics on the early Earth: Limitations imposed
314 by strength and buoyancy of subducted lithosphere. *Lithos* **103**, 217-235 (2008) .
- 315 26. Gerya, T.V., Bercovici, D. & Becker, T.W. Dynamic slab segmentation due to brittle-
316 ductile damage in the outer rise. *Nature* **599**, 245-250 (2021).

- 317 27. Allègre, C.J. Limitation on the mass exchange between the upper and lower mantle: the
318 evolving convection regime of the Earth. *Earth Planet. Sci. Lett.* **150**, 1-6 (1997) .
- 319 28. Martin, H. Adakitic magmas: modern analogues of Archean granitoids. *Lithos* **46**, 411-429
320 (1999) .
- 321 29. Hoffmann, J.E. et al. Mechanisms of Archean crust formation inferred from high-precision
322 HFSE systematics in TTGs. *Geochim. Cosmochim. Acta* **75**, 4157-4178 (2011).
- 323 30. Nagel, T.J., Hoffmann, J.E. & Münker, C. Generation of Eoarchean tonalite-trondhjemite-
324 granodiorite series from thickened mafic arc crust. *Geology* **40**, 375-378 (2012).
- 325 31. Hoare, L. et al. Melt chemistry and redox conditions control titanium isotope fractionation
326 during magmatic differentiation. *Geochim. Cosmochim. Acta* **282**, 38-54 (2020).
- 327 32. Zhao, X. et al. Titanium isotopic fractionation during magmatic differentiation. *Contrib.*
328 *Miner. Petrol.* **175**, 67 (2020).
- 329 33. Greber, N.D., Dauphas, N., Puchtel, I.S., Hofmann, B.A. & Arndt, N.T. Titanium stable
330 isotopic variations in chondrites, achondrites and lunar rocks. *Geochim. Cosmochim. Acta*
331 **213**, 534-552 (2017).
- 332 34. Deng, Z. et al. Lack of resolvable titanium stable isotopic variations in bulk chondrites.
333 *Geochim. Cosmochim. Acta.* **239**, 409-419 (2018).
- 334 35. Williams, N.H., Fehr, M.A., Parkinson, I.J., Mandl, M.B. & Schönbacher, M. Titanium
335 isotope fractionation in solar materials. *Chem. Geol.* **568**: 120009 (2021).
- 336 36. Arndt, N. Komatiites, kimberlites, and boninites. *J. Geophys. Res. Solid Earth* **108**. (2003)
337 DOI: 10.1029/2002JB002157
- 338 37. Sossi, P.A. et al. Petrogenesis and geochemistry of Archean komatiites. *J. Petrol.* **57**, 147-
339 184 (2016).
- 340 38. Rzehak, L.J.A. et al. The redox dependence of titanium isotope fractionation in synthetic
341 Ti-rich lunar melts. *Contrib. Mineral. Petrol.* **176**, 19 (2021).

- 342 39. Anguelova, M., Fehr, M.A., Takazawa, E. & Schönbacher, M. Titanium isotope
343 heterogeneity in the Earth's mantle: A case study of the Horoman peridotite massif.
344 *Geochim. Cosmochim. Acta* **335**, 356-368 (2022).
- 345 40. Wang, W., Huang, S., Huang, F., Zhao, X. & Wu, Z. Equilibrium inter-mineral titanium
346 isotope fractionation: Implication for high-temperature titanium isotope geochemistry.
347 *Geochim. Cosmochim. Acta* **269**, 540-553 (2020).
- 348 41. Bédard, J.H. Stagnant lids and mantle overturns: Implications for Archean tectonics,
349 magmagenesis, crustal growth, mantle evolution, and the start of plate tectonics.
350 *Geoscience Frontiers* **9**, 19-49 (2018).
- 351 42. Tusch, J. et al. Long-term preservation of Hadean protocrust in Earth's mantle. *Proc. Natl.*
352 *Acad. Sci. U.S.A.* **119**, e2120241119 (2022).
- 353 43. Taylor, S.R. & McLennan, S.M. The continental crust: its composition and evolution.
354 Blackwell, Oxford, 312 pp (1985).
- 355 44. Dhuime, B., Hawkesworth, C.J., Cawood, P.A. & Storey, C.D. A change in the
356 geodynamics of continental growth 3 billion years ago. *Science* **335**, 1334-1336 (2012).
- 357 45. Dhuime, B., Hawkesworth, C.J., Delavault, H. & Cawood, P.A. Rates of generation and
358 destruction of the continental crust: implications for continental growth. *Phil. Trans. R. Soc.*
359 *A* **376**. (2018) DOI: 10.1098/rsta.2017.0403.
- 360 46. White, W.M. Oceanic Island basalts and mantle plumes: the geochemical perspectives. *Ann.*
361 *Rev. Earth Planet. Sci.* **38**, 133-160 (2010).
- 362 47. Jackson, M.G. et al. The return of subducted continental crust in Samoan lavas. *Nature* **448**,
363 684-687 (2007).
- 364 48. Workman, R.K. & Hart, S.R. Major and trace element composition of the depleted MORB
365 mantle (DMM). *Earth Planet. Sci. Lett.* **231**, 53-72 (2005).

- 366 49. Hofmann, A.W., Jochum, K.P., Seufert, M. & White, W.M. Nb and Pb in oceanic basalts:
367 New constraints on mantle evolution. *Earth Planet. Sci. Lett.* **79**: 33-45 (1986) .
- 368 50. Hofmann, A.W. & White, W.M. Mantle plumes from ancient oceanic crust. *Earth Planet.*
369 *Sci. Lett.* **57**, 421-436 (1982).
- 370 51. Chauvel, C., Lewin, E., Carpentier, M., Arndt, N.T. & Marini, J.C. Role of recycled oceanic
371 basalt and sediment in generating the Hf-Nd mantle array. *Nat. Geosci.* **1**, 64-67 (2007).
- 372 52. Bouhifd, M.A., Jephcoat, A.P., Heber, V.S. & Kelley, S.P. Helium in Earth's early core.
373 *Nat. Geosci.* **6**, 982-986 (2013).
- 374 53. Roth, A.S.G. et al. The primordial He budget for the Earth set by percolative core formation
375 in planetesimals. *Geochem. Perspect. Lett.* **9**, 26-31 (2019).
- 376 54. Rizo, H. et al. ¹⁸²W evidence for core-mantle interaction in the source of mantle plumes.
377 *Geochem. Persp. Let.* **11**: 6-11 (2019).
- 378 55. Jackson, M.G. et al. Ancient helium and tungsten isotopic signatures preserved in mantle
379 domains least modified by crustal recycling. *Proc. Natl. Acad. Sci. U.S.A.* **117**, 30993-
380 31001 (2020).
- 381 56. Mundl-Petermeier, A. et al. Anomalous ¹⁸²W in high ³He/⁴He oceanic island basalts:
382 Fingerprints of Earth's core? *Geochim. Cosmochim. Acta* **271**, 194-211 (2020).
- 383 57. Debaille, V. et al. Stagnant-lid tectonics in early Earth revealed by ¹⁴²Nd variations in late
384 Archean rocks. *Earth Planet. Sci. Lett.* **373**, 83-92 (2013).
- 385 58. Saji, N.S. et al. Hadean geodynamics inferred from time-varying ¹⁴²Nd/¹⁴⁴Nd in the early
386 Earth rock record. *Geochem. Persp. Let.* **7**, 43-48 (2018).
- 387 59. Zegers, T.E. & van Keken, P.E. Middle Archean continent formation by crustal
388 delamination. *Geology* **29**, 1083-1086 (2001) .
- 389 60. Johnson, T.E., Brown, M., Gardiner, N.J., Kirkland, C.L., Smithies, R.H. Earth's first stable
390 continents did not form by subduction. *Nature* **543**, 239-242 (2017) .

- 391 61. Deng, Z. et al. An oceanic subduction origin for Archean granitoids revealed by silicon
392 isotopes. *Nature Geosci.* **12**, 774-778 (2019).
- 393 62. Antonelli, M.A. et al. Calcium isotope evidence for early Archaean carbonates and
394 subduction of oceanic crust. *Nat. Commun.* **12**, 2534 (2021).
- 395 63. Ringwood, A.E. & Irifune, T. Nature of the 650-km seismic discontinuity: implications for
396 mantle dynamics and differentiation. *Nature* **331**, 131-136 (1988).
- 397

398 **Figure Captions**

399 **Figure 1** Mass-dependent Ti isotopic variations in bulk chondrites and Archean, Proterozoic
400 and modern terrestrial mantle-derived rocks from this study and literature^{3,4,6,7,31,32}. See the full
401 dataset in the Extended Data Tables. Note that all the plotted terrestrial mantle-derived rocks
402 are identified to be devoid of Fe-Ti oxide fractionation. The Archean mantle-derived rocks
403 from this study and ref. 4 have been arranged into three groups based on the formation ages
404 (~3.8-3.5 Ga, ~3.4-3.3 Ga and ~2.8-2.7 Ga), which show a progressive enrichment in the light
405 Ti isotopes with age. The ~2.0 Ga data are from the Kangâmiut dyke samples ([Southwest](#)
406 [Greenland](#)) in this study. Also shown are the data of ~3.6-2.9 Ga tonalite-trondhjemite-
407 granodiorite (TTG) rocks from this study and refs. 5 and 7, and that of modern N-MORBs from
408 refs. 3 and 4. The box on each group of data defines the 25-75% percentiles with the medium
409 value marked in the box and the whisker standing for 0-100% percentiles excluding outliers.
410 Abbreviations: N-MORBs, normal-type mid-ocean ridge basalts; OIBs, oceanic island basalts.

411 **Figure 2** Continental crust extraction and the evolution of Ti isotopic composition in mantle-
412 derived rocks. Chondrites and terrestrial mantle-derived rocks are shown in groups as defined
413 in Fig. 1 with individual data points plotting as grey dots. The continental crust growth models
414 from [Taylor and McLennan](#)⁴³ and [Dhuime et al.](#)⁴⁴ are shown on the upper plot. Crustal recycling
415 models were made to quantify the potential Ti isotopic effects in the mantle from continental
416 crust formation, where f represents the fraction of Earth's mantle to equilibrate with recycling
417 crustal melting residues, and k stands for the total mass of continental crust ever produced
418 throughout the geologic history after normalisation onto its present mass (i.e., ~0.55% of the
419 BSE). See equations 13 and 14 and the related descriptions in **Methods** for details of the models.
420 The box on each group of data defines the 25-75% percentiles with the medium value marked
421 in the box and the whisker standing for 0-100% percentiles excluding outliers. Abbreviations:
422 N-MORBs, normal-type mid-ocean ridge basalts; OIBs, oceanic island basalts.

423 **Figure 3** Sampling of a primordial mantle reservoir by mantle plume as evidenced by Ti and
424 Sr isotopic records of the modern oceanic island basalts (OIBs) from the Iceland, Samoa, and
425 Caroline hotspots. Data of the OIB samples from Cape Verde and Azores in ref. 3 were shown
426 as white circles. The N-MORB and E-MORB samples from refs. 3 and 4 are shown, where the
427 N-MORB samples without available Sr isotope data have been assumed to have $^{87}\text{Sr}/^{86}\text{Sr} =$
428 0.7025 . The pink dotted trajectories describe the effects from mixing in increments of 0.2% the
429 ancient marine sediments or continental crust material with $\delta^{49}\text{Ti} = +0.200\%$ ^{5,6}, and $^{87}\text{Sr}/^{86}\text{Sr}$
430 $= 0.740$ ⁴⁷ into a modern depleted MORB mantle source with $^{87}\text{Sr}/^{86}\text{Sr} = 0.7025$ ⁴⁸ and $\delta^{49}\text{Ti} =$
431 $+0.001\%$ ^{3,4}, or into a mantle source with $^{87}\text{Sr}/^{86}\text{Sr} = 0.7035$ and a primordial mantle $\delta^{49}\text{Ti}$ of
432 $+0.052\%$. Addition of recycled melting residues would lead to lower $\delta^{49}\text{Ti}$ values in N-MORBs
433 and some of the OIBs. Abbreviations: N- or E-MORBs, normal- or enriched-type mid-ocean
434 ridge basalts.

435 **Methods**

436 ***Samples***

437 The chondrite samples analysed in this study include 1 CI (Orgueil), 2 CV (NWA 2364 and
438 Allende CAI-free matrix), 6 CM (Cold Bokkeveld, Murray, Murchison, Bells, Maribo and
439 NWA 4428), 2 CO (NWA 1232 and NWA 763), 1 CH (SaU 290), 2 CK (NWA 1559 and NWA
440 1563), 4 CR (NWA 530, NWA 1180, NWA 6043 and NWA 801), 1 EH (SaH 97159), 3 L
441 (NWA 5697, Bovedy and Hedjaz) and 2 LL (Ragland and Talbachat n'aït Isfoul).

442 The Archean to Proterozoic samples from three locations were also studied, comprising i) five
443 ~3.8 Ga pillow-textured metabasalt/metagabbro samples (PB-1, PB-2, PB-3, GB-1 and MG-
444 1), one ~3.8 Ga Amitsoq gneiss (SD-2), eight ~3.4 Ga doleritic samples of the Ameralik dyke
445 swarm (AM-1, AM-2, AM-8, AM-9, AM-10, AM-12, AM-14 and AM-16) and six ~2.0 Ga
446 Kangâmiut dyke samples (430931, 430970, 430981, 430988, 432108 and 432122) from
447 [Southwest Greenland](#), ii) two ~3.48 Ga komatiite (1973-543 and 1973-547) and four ~3.48 Ga
448 basaltic komatiite samples (1973-544, 1973-545, 1973-546 and 1973-730) of the Komati
449 Formation as well as three ~3.33 Ga tholeiitic basalt samples (1973-549, 1973-555 and 1973-
450 733) of the Kromberg Formation from the [KAAPVAAL CRATON](#) in South Africa, and iii) three ~2.7
451 Ga Pyke Hill komatiite samples (1990-63, 1990-65 and 1990-67) in Munro Township from the
452 Abitibi greenstone belt in Canada. The ~3.8 Ga [Isua](#) metabasalts and the ~3.45 Ga Ameralik
453 dyke samples have been shown to have positive ^{142}Nd excesses of $+10.5 \pm 0.7$ and $+4.9 \pm 0.5$,
454 respectively⁵⁸. The reduced ^{142}Nd excesses in the Ameralik dyke samples relative to the older
455 metabasalts have been attributed to a recycling of Earth's primordial crust into the upper
456 mantle⁵⁸.

457 In addition to the chondrite and Archean/Proterozoic samples, we selected 21 modern oceanic
458 island basalts (OIBs) for study, comprising i) ICE-14-16, ICE-14-18, ICE-12-27, ICE-14-29,
459 ICE-14-32A and 408616 from Iceland hotspot⁵⁵, ii) KOS-13-4 and KOS-13-19 from the

460 Caroline hotspot⁶⁴, and iii) OFU-04-05, OFU-05-01 and OFU-05-18 of the Ofu Island⁶⁵, T30,
461 T33, T44 and T45 of the Ta'u Island⁶⁵, and AVON3-63-2, AVON3-70-9, AVON3-71-22,
462 AVON3-73-1 and AVON3-77-1 of the Vailulu'u Island⁶⁶ from the Samoa hotspot. Most of the
463 analysed modern OIB samples have been characterised for both chemical (major and trace
464 elements) and radiogenic isotope (Sr-Nd-Pb-He-W) compositions in literature^{55-56,64-66}. Most
465 of the analysed OIB samples have higher $^3\text{He}/^4\text{He}$ ratios (up to 38.7 Ra, where Ra represents a
466 normalisation onto the $^3\text{He}/^4\text{He}$ ratio of atmosphere) compared to that of N-MORBs (~8 Ra)
467 ^{55,64-66}. These OIB samples also have resolvable negative u^{182}W values of down to -13.8 ± 3.3
468 ppm^{16,56}.

469 Although fractional crystallisation of Fe-Ti oxides can quickly lead to increasing $\delta^{49}\text{Ti}$ values
470 for evolved mafic lavas^{3,6,7,31,32}, we argue that the mantle-derived rocks in this study are devoid
471 of Fe-Ti oxide fractionation based on two observations: i) while at fayalite-magnetite-quartz
472 (FMQ) buffer, Fe-Ti oxides normally start crystallising at late stage of magma differentiation⁶⁷
473 ($\text{MgO} < 5 \text{ wt}\%$), the measured samples are with high MgO contents of $> 5.80 \text{ wt}\%$, except for
474 sample ICE-14-16 with $\text{MgO} = 5.02 \text{ wt}\%$; and ii) the lavas from the same age groups or the
475 same oceanic islands did not show resolvable increase in $\delta^{49}\text{Ti}$ with the decreasing MgO
476 contents (Extended Data Fig. 1b). We also note that some OIB samples contain the earlier
477 crystallized olivine phenocrysts that would lead to much higher MgO contents, which however
478 should have negligible effects on the Ti isotopic compositions of the studied samples in a whole
479 rock scale due to the low TiO_2 contents in olivine.

480 ***Sample dissolution and chromatographic purification of Ti***

481 Powders of samples were weighed into precleaned Savillex beakers and dissolved with
482 mixtures of 22 M HF and 14 M HNO_3 acids in a 2:1 volume ratio. The modern OIBs and four
483 reference materials (i.e., BHVO-2, BCR-2, AGV-2, and BIR-1) were digested on hotplate at
484 120 °C for four days. Note that all chondrite and Archean ultramafic/mafic rock samples were

485 digested in Parr bomb vessels at 220 °C for three days to ensure full dissolution of refractory
486 phases. Dissolution of the dried samples in 5-10 mL 6 M HCl at 120 °C and evaporation were
487 carried out multiple times to decompose the fluorides formed from HF digestion until clear
488 solutions were obtained. Aliquot of each sample was taken and spiked with a prepared ⁴⁷Ti-
489 ⁴⁹Ti double spike to determine in advance the Ti concentration using an iCAP RQ inductively-
490 coupled-plasma mass spectrometer (ICP-MS) at the Centre for Star and Planet Formation
491 (StarPlan) at the University of Copenhagen. Afterwards, aliquots containing 6 µg Ti were taken
492 and mixed with a ⁴⁷Ti-⁴⁹Ti double spike as described previously in ref. 34. The dried mixtures
493 were dissolved with 6 M HCl at 120 °C overnight to ensure sample-spike equilibration.
494 Titanium was separated from matrix elements following a three-step purification protocol using
495 AG1x8 (200-400 meshes) and DGA resins^{34,68}, i.e., first to separate Fe with 6 M HCl elution
496 on AG1x8 columns, second to remove most of major and trace elements via 12 M HNO₃ elution
497 and to collect Ti with Milli-Q H₂O on DGA columns, and third to purify Ti from the remaining
498 matrix elements with 4 M HF cleaning on AG1x8 columns. An extra DGA pass can be carried
499 out to remove trace amounts of Ca and Cr in the final Ti cuts. To destroy the resin particles and
500 organics from column chemistry, the Ti cuts were treated with 14 M HNO₃ at 120 °C before
501 storage in 0.5 M HNO₃ + 0.01 M HF acids.

502 *Neoma multi-collector inductively-coupled-plasma mass spectrometry (MC-ICP-MS)*

503 Titanium isotopic compositions of the purified samples were measured using the ThermoFisher
504 Neoma MC-ICP-MS. Sample solutions with 500-800 ppb Ti dissolved in 0.5 M HNO₃ + 0.01
505 M HF were introduced into the MC-ICP-MS via an APEX HF desolvating nebulizer from
506 Elemental Scientific, and a sapphire injector was used instead of the quartz-made injector to
507 reduce the production of silicon fluorides from the use of HF solvent. An actively cooled
508 membrane desolvation (ACM) component was attached after the APEX to suppress oxide
509 formation and to stabilise the signals, and N₂ gas in a flow rate of a few mL/min was added to

510 improve the sensitivity. Such a setting typically provides an intensity of ~ 15 V on $^{48}\text{Ti}^+$ at an
511 uptake rate of ~ 50 uL/min for a 600 ppb Ti solution under a medium mass resolution mode.
512 The increased mass dispersion of the Neoma relative to earlier generation instruments allows
513 for a simultaneous monitor of $^{43}\text{Ca}^+$ (L5), $^{44}\text{Ca}^+$ (L4), $^{46}\text{Ti}^+$ (L3), $^{47}\text{Ti}^+$ (L1), $^{48}\text{Ti}^+$ (C), $^{49}\text{Ti}^+$
514 (H1), $^{50}\text{Ti}^+$ (H2), $^{51}\text{V}^+$ (H3), $^{52}\text{Cr}^+$ (H4), and $^{53}\text{Cr}^+$ (H5) species in a single collector
515 configuration. The medium mass resolution mode on the Neoma (i.e., $M/\Delta M = \sim 7000$) can
516 resolve the major molecular isobaric interferences on the measured masses (e.g., $^{28}\text{Si}^{16}\text{O}^+$ on
517 $^{44}\text{Ca}^+$, $^{28}\text{Si}^{19}\text{F}^+$ on $^{47}\text{Ti}^+$, and $^{36}\text{Ar}^{14}\text{N}^+$ on $^{50}\text{Ti}^+$). Measuring intensities on $^{44}\text{Ca}^+$, $^{51}\text{V}^+$ and $^{53}\text{Cr}^+$
518 with those of Ti allows for a high-precision correction of the related isobaric interferences. To
519 account for instrumental mass bias on the measurements from different sessions, a strict
520 standard-sample bracketing protocol was used for all the MC-ICP-MS sessions in this study,
521 i.e., to analyse the OL-Ti standard solution before and after every sample analysis. Each
522 analysis of the standard or samples comprise 100 cycles with 8 s integration time. On peak
523 zeros were measured before each sample/standard analyses in the same 0.5 M HNO_3 + 0.01 M
524 HF solution used to dissolve the sample/standard for 75 cycles with 8 s integration time. The
525 typical background for the measurements is ~ 2 -4 mV on $^{48}\text{Ti}^+$. To evaluate data reproducibility,
526 each sample has been normally analysed 4-8 times, and four reference materials (i.e., BHVO-
527 2, BCR-2, AGV-2, and BIR-1) have been processed multiple times in parallel with the
528 unknown samples.

529 ***Concomitant derivation of Ti stable isotope composition and nucleosynthetic component***
530 ***from double spike measurements***

531 An accurate determination of the Ti stable isotope composition in meteoritic samples via a
532 double spike technique requires knowledge of the nucleosynthetic composition of the samples
533 for correction. In the past, a separate protocol was needed for measurements of Ti
534 nucleosynthetic components, i.e., to analyse the samples purified without introducing a spike⁶⁸

535 ⁷⁰. Since this approach is time consuming, previous Ti isotope studies^{33,34} have relied on
 536 literature values of the same meteorites or the same meteorite groups for correction. However,
 537 this is non-ideal as it can introduce artifacts on the Ti stable isotope composition if
 538 discrepancies in Ti nucleosynthetic component exist between the new digestion aliquots of
 539 meteorites and those in literature.

540 It is however noteworthy that after normalisation onto the ⁴⁹Ti/⁴⁷Ti ratio, meteorites in bulk
 541 exhibit anomalies mainly on ⁴⁶Ti and ⁵⁰Ti (refs. 69 and 70), which are correlated following a
 542 relation of $\epsilon^{46}\text{Ti} = (0.184 \pm 0.007) \times \epsilon^{50}\text{Ti} + (0.025 \pm 0.009)$ (ref. 71), where an epsilon notation
 543 is used to describe the magnitude of these isotopic anomalies. In this case, it is possible to
 544 derive both the Ti stable isotope composition and the nucleosynthetic component in samples
 545 from the measured results of a sample-spike mixture via the following procedures, with the
 546 standard composition (i.e., $R_{\text{standard}}^{46/47}$, $R_{\text{standard}}^{48/47}$, $R_{\text{standard}}^{49/47}$ and $R_{\text{standard}}^{50/47}$) and the ⁴⁷Ti-⁴⁹Ti double
 547 spike composition (i.e., $R_{\text{spike}}^{46/47}$, $R_{\text{spike}}^{48/47}$, $R_{\text{spike}}^{49/47}$ and $R_{\text{spike}}^{50/47}$) calibrated in advance:

548 i) The interference-corrected ⁴⁶Ti/⁴⁷Ti, ⁴⁸Ti/⁴⁷Ti and ⁴⁹Ti/⁴⁷Ti ratios from an analysis of either
 549 OL-Ti standard or unknown samples can be used for a primary double spike inversion to obtain
 550 solutions for the three unknowns λ (i.e., the proportion of ⁴⁷Ti from the ⁴⁷Ti-⁴⁹Ti double spike
 551 in the sample-spike mixture), α (i.e., the natural mass fractionation factor) and β (i.e., the
 552 instrumental mass fractionation factor) as defined in a set of three non-linear equations⁷²:

$$553 F_i(\lambda, \alpha, \beta, n, m, T) = \lambda T_i + (1 - \lambda)n_i e^{-\alpha P_i} - m_i e^{-\beta P_i} = 0, \quad (1)$$

554 where n , m and T represent the standard, the sample-spike mixture, and the ⁴⁷Ti-⁴⁹Ti double
 555 spike, respectively, and each of them further comprises three known or measured Ti isotopic
 556 ratios (i.e., ⁴⁶Ti/⁴⁷Ti, ⁴⁸Ti/⁴⁷Ti and ⁴⁹Ti/⁴⁷Ti), and P_i stands for a natural log of the atomic masses
 557 included in the selected isotope ratio i , e.g., $P_i = \ln(45.9526316/46.9517631)$ for the ⁴⁶Ti/⁴⁷Ti
 558 ratio.

559 ii) The $^{50}\text{Ti}/^{47}\text{Ti}$ ratio of the sample ($R_{\text{sample}}^{50/47}$) can be derived from the measured $^{50}\text{Ti}/^{47}\text{Ti}$ ratio
 560 of the mixture ($R_{\text{mixture}}^{50/47}$) and that of the ^{47}Ti - ^{49}Ti double spike ($R_{\text{spike}}^{50/47}$) using the defined λ and
 561 β values:

$$562 \quad R_{\text{sample}}^{50/47} = [R_{\text{mixture}}^{50/47} \times e^{-\beta \times \ln(m_{50}/m_{47})} - \lambda \times R_{\text{spike}}^{50/47}] / (1 - \lambda), \quad (2)$$

563 iii) Afterwards, in a case that instrumental mass bias follows the exponential mass fractionation
 564 law as assumed in equations 1 and 2, deviation of the $^{50}\text{Ti}/^{47}\text{Ti}$ ratio of sample ($R_{\text{sample}}^{50/47}$) from
 565 that of the standard composition ($R_{\text{standard}}^{50/47}$) would be a combined result of the isotopic anomaly
 566 on ^{50}Ti and the mass-dependent isotopic fractionation from natural processes, where the
 567 magnitude of the latter can be quantified from the α value of the sample for correction. In this
 568 case, the ^{50}Ti anomaly of the sample in an epsilon notation ($\epsilon^{50}\text{Ti}$) would be the same as the
 569 preliminary calculated values (i.e., $\epsilon^{50}\text{Ti}_{\text{prelim}}$):

$$570 \quad \epsilon^{50}\text{Ti}_{\text{prelim}} = [R_{\text{sample}}^{50/47} \times e^{-\alpha \times \ln(m_{50}/m_{47})} / R_{\text{standard}}^{50/47} - 1] \times 10,000, \quad (3)$$

571 where m_{47} and m_{50} stand for the atomic masses of ^{47}Ti and ^{50}Ti , respectively.

572 In the other case that the instrumental mass bias may slightly differ from the exponential mass
 573 fractionation law, mass-independent Ti isotopic effects would be created from double spike
 574 inversion, and therefore a secondary normalisation onto the bracketing OL-Ti standards would
 575 be necessary to obtain the correct ^{50}Ti anomalies for unknown samples, where a spline with the
 576 minimal MSWD value on the $\epsilon^{50}\text{Ti}_{\text{prelim}}$ values of the OL-Ti standard can be used for the
 577 normalisation:

$$578 \quad \epsilon^{50}\text{Ti} = \epsilon^{50}\text{Ti}_{\text{prelim-sample}} - \epsilon^{50}\text{Ti}_{\text{OL-Ti spline}}, \quad (4)$$

579 iv) It is however notable that the primary double spike inversion includes no correction of ^{46}Ti
 580 anomaly. Following equation 4, a $\epsilon^{50}\text{Ti}$ value can be obtained for an unknown sample from
 581 averaging the results from duplicate measurements, after which a $\epsilon^{46}\text{Ti}$ value can be further
 582 inferred based on the correlation between $\epsilon^{46}\text{Ti}$ and $\epsilon^{50}\text{Ti}$, i.e., $\epsilon^{46}\text{Ti} = (0.184 \pm 0.007) \times \epsilon^{50}\text{Ti}$

583 + (0.025 ± 0.009)(ref. 71). An ideal way to correct for ⁴⁶Ti anomaly is to create an equivalent
 584 effect on the standard composition before double spike inversion:

$$585 \quad (R_{\text{standard}}^{46/47})_{\text{new}} = R_{\text{standard}}^{46/47} \times \left(\frac{\epsilon^{46}\text{Ti}}{10,000} + 1 \right), \quad (5)$$

586 v) As the correction of ⁴⁶Ti anomaly would affect the calculated λ , α and β values from double
 587 spike inversion and then the calculated $\epsilon^{46}\text{Ti}$ and $\epsilon^{50}\text{Ti}$ values, an iteration of procedures i) to
 588 iv) needs to be carried out using the updated standard composition, and the $\epsilon^{50}\text{Ti}$ values for
 589 unknown samples normally converge after 4 or 5 iterations. The preliminary mass-dependent
 590 Ti isotopic fractionations (reported as a delta notation on the ⁴⁹Ti/⁴⁷Ti ratio relative to the
 591 standard composition) can be obtained from the α :

$$592 \quad \delta^{49}\text{Ti}_{\text{prelim}} = \left(e^{-\alpha \times \ln(m_{49}/m_{47})} - 1 \right) \times 1,000, \quad (6)$$

593 where m_{47} and m_{49} stand for the atomic masses of ⁴⁷Ti and ⁴⁹Ti, respectively. In a case that the
 594 instrumental mass fractionation bias did not follow exactly an exponential mass fractionation
 595 law, a secondary normalisation onto the bracketing OL-Ti standard is necessary to obtain the
 596 correct mass-dependent Ti isotopic fractionations for unknown samples, where a spline with
 597 the minimal MSWD value on the $\delta^{49}\text{Ti}_{\text{prelim}}$ values of the OL-Ti standard can be used for the
 598 normalisation:

$$599 \quad \delta^{49}\text{Ti} = \delta^{49}\text{Ti}_{\text{prelim-sample}} - \delta^{49}\text{Ti}_{\text{OL-Ti spline}}, \quad (7)$$

600 ***Propagation of uncertainty from anomaly correction***

601 The uncertainties from the derivation of ⁴⁶Ti anomalies from the measured ⁵⁰Ti anomalies and
 602 the subsequent correction need to be propagated onto the results. Main uncertainties on the
 603 derived ⁴⁶Ti anomalies should come from i) uncertainties on the ⁵⁰Ti measurements, and ii)
 604 uncertainties from the assumed relation between $\epsilon^{46}\text{Ti}$ and $\epsilon^{50}\text{Ti}$, i.e., $\epsilon^{46}\text{Ti} = (0.184 \pm 0.007) \times$
 605 $\epsilon^{50}\text{Ti} + (0.025 \pm 0.009)$. We consider that the 2se value of the $\epsilon^{50}\text{Ti}_{\text{prelim}}$ values from duplicate
 606 measurements of each sample to represent the uncertainty on the ⁵⁰Ti measurements for this

607 sample, i.e., $\sigma(\epsilon^{50}\text{Ti}_{\text{prelim}})$. The uncertainty on the inferred ^{46}Ti anomaly can be approximated
 608 to:

$$609 \quad \sigma(\epsilon^{46}\text{Ti}) \approx \sqrt{[\sigma(\epsilon^{50}\text{Ti}_{\text{prelim}}) \times 0.184]^2 + 0.009^2}, \quad (8)$$

610 The effects from ^{46}Ti correction on $\delta^{49}\text{Ti}$ and $\epsilon^{50}\text{Ti}$ values can be empirically evaluated via
 611 assigning various $\epsilon^{46}\text{Ti}$ values for correction within the data processing protocol described
 612 above, which follows linear equations of the assigned $\epsilon^{46}\text{Ti}$ value:

$$613 \quad \delta^{49}\text{Ti}_{\text{corr}} - \delta^{49}\text{Ti}_{\text{uncorr}} \approx 0.108 \times \epsilon^{46}\text{Ti}, \quad (9)$$

$$614 \quad \epsilon^{50}\text{Ti}_{\text{corr}} - \epsilon^{50}\text{Ti}_{\text{uncorr}} \approx -0.96 \times \epsilon^{46}\text{Ti}, \quad (10)$$

615 The uncertainty on the derived $\epsilon^{46}\text{Ti}$ value from equation 8 can be further propagated onto the
 616 $\delta^{49}\text{Ti}$ and $\epsilon^{50}\text{Ti}$ results:

$$617 \quad \sigma(\delta^{49}\text{Ti}) \approx \sqrt{[\sigma(\epsilon^{46}\text{Ti}) \times 0.108]^2 + [\sigma(\delta^{49}\text{Ti}_{\text{prelim}})]^2}, \quad (11)$$

$$618 \quad \sigma(\epsilon^{50}\text{Ti}) \approx \sqrt{[\sigma(\epsilon^{46}\text{Ti}) \times (-0.96)]^2 + [\sigma(\epsilon^{50}\text{Ti}_{\text{prelim}})]^2}, \quad (12)$$

619 Note that the pooled uncertainties on the $\epsilon^{50}\text{Ti}_{\text{prelim}}$ and $\delta^{49}\text{Ti}_{\text{prelim}}$ values from duplicate
 620 measurements are ± 0.15 and $\pm 0.010\%$, respectively. Substituting these values into equations
 621 8, 11 and 12 shows that the propagated uncertainties from anomaly correction are negligible
 622 relative to the uncertainties on $\epsilon^{50}\text{Ti}_{\text{prelim}}$ and $\delta^{49}\text{Ti}_{\text{prelim}}$.

623 ***Results and data reproducibility***

624 Although simulation shows that the utilisation of a ^{47}Ti - ^{49}Ti double spike provides optimally
 625 small errors on the results for a large spiking range ($f_{\text{sample}} = 0.20$ - 0.80 where f_{sample} stands for
 626 the sample fraction in the sample-spike mixture⁷³), in practice there may be systematic offsets
 627 in the calculated $\delta^{49}\text{Ti}$ value when acquiring data at different spiking ratios, e.g., up to $\sim 0.18\%$
 628 offsets for the spiked Ti Alfa Aesar aliquots that have f_{sample} values between 0.20 and 0.80 (ref.
 629 35). Despite the magnitude of the offsets at different spiking ratios depends on the calibration

630 of the standard composition and the used ^{47}Ti - ^{49}Ti double spike at different laboratories, it is
631 worthy to scrutinise the effects and if necessary, optimize the f_{sample} values between the samples
632 and the bracketing standard. Except for the Cold Bokkeveld sample ($f_{\text{sample}} = 0.470$), all the
633 samples in this study have the f_{sample} values within a small range (0.409-0.454), which are in a
634 close match with that of the used bracketing OL-Ti standard solutions ($f_{\text{sample}} = 0.43$ -0.44).
635 Multiple runs of three reference materials (i.e., BHVO-2, BCR-2, and AGV-2) and two
636 chondrites (Murchison and Murray) at different spiking ratios show that within a f_{sample} range
637 of 0.409-0.454, no systematic offset relative to the bracketing OL-Ti standard ($f_{\text{sample}} = 0.43$ -
638 0.44) was resolved at a precision of ± 0.15 for $\epsilon^{50}\text{Ti}$ and of $\pm 0.010\text{‰}$ for $\delta^{49}\text{Ti}$.
639 Multiple runs of reference materials BHVO-2, BCR-2, and AGV-2 provide $\delta^{49}\text{Ti}$ values of
640 $+0.024 \pm 0.010\text{‰}$ ($n = 9$, 2SD), $+0.001 \pm 0.006\text{‰}$ ($n = 8$, 2SD), and $+0.097 \pm 0.013\text{‰}$ ($n = 4$,
641 2SD), respectively. These are within uncertainty identical to the previously recommended
642 values in literature^{3,4,32,34,35}. With respect to anomaly measurements, all the duplicate runs of
643 reference materials BHVO-2, BCR-2, AGV-2, and BIR-1 give a mean $\epsilon^{50}\text{Ti}$ value of $-0.07 \pm$
644 0.14 ($n = 19$, 2SD). The consistency of the $\delta^{49}\text{Ti}$ and $\epsilon^{50}\text{Ti}$ values from multiple runs of the
645 same samples suggests for a long-term external precision of $\pm 0.010\text{‰}$ and ± 0.15 , respectively
646 on the $\delta^{49}\text{Ti}$ and $\epsilon^{50}\text{Ti}$ data from this study. It is also noteworthy that the $\epsilon^{50}\text{Ti}$ values of both
647 terrestrial reference materials and chondrite meteorites including Murchison, Orgueil, NWA
648 5697, and SaH 97159 are consistent with the values acquired previously in refs. 69 and 70 via
649 a non-spike method (Extended Data Fig. 2), which demonstrate that the $\epsilon^{50}\text{Ti}$ results derived
650 from double spike measurements in this study are accurate at the claimed precision.

651 ***Precise and accurate determination of the $\delta^{49}\text{Ti}$ average for whole-rock chondrites***

652 There is significant scatter of the $\delta^{49}\text{Ti}$ data reported for whole-rock chondrites in the literature,
653 for instance a $\delta^{49}\text{Ti}$ average of $+0.008 \pm 0.039\text{‰}$ ($n = 16$, 2SD) from Greber et al.³³, of $+0.071$
654 $\pm 0.085\text{‰}$ ($n = 22$, 2SD) from Deng et al.³⁴ and of $+0.047 \pm 0.071\text{‰}$ ($n = 6$, 2SD) from Williams

655 et al.³⁵. However, we note that significant offsets in $\delta^{49}\text{Ti}$ (up to 0.100‰) were observed
656 between lithium metaborate fusion digestions of the same komatiite and eucrite powders (e.g.,
657 501-1, 501-8, M657, M663, M666, M712, Lakangaon, and Ibitira; Extended Data Fig. 3a) in
658 Greber *et al.*³³, and the authors have ascribed the discrepancy to a lack of equilibration of the
659 sample with the double spike that results in lower $\delta^{49}\text{Ti}$ values³³.

660 For the digestion or spiking protocols involving HF acids, fluoride formation hampers either
661 full sample dissolution or sample-spike equilibration. Here we have carried out experiments to
662 evaluate the potential effects from fluorides on the $\delta^{49}\text{Ti}$ data in this study as follows:

663 i) A ~1425 mg chip of NWA 5697 (L3) meteorite was crushed into a fine powder (NWA 5697-
664 B), and six aliquots with masses of 83 to 99 mg (-01, -02, -03, -04, -05, and -06) were digested
665 following the typical Parr Bomb digestion procedure. Aliquots containing ~6 μg Ti were taken
666 from ‘-1’ and ‘-2’ digestions and spiked in 6 M HCl on a hot plate at 120 °C, whereas the other
667 four whole digestions were spiked and placed into Parr Bomb with 14 M HNO₃ acids at 190
668 °C for a day, at which condition fluorides should decompose. The six experiments provide
669 consistent $\delta^{49}\text{Ti}$ values ($+0.032 \pm 0.004\text{‰}$, $n = 6$, 2SD) that agrees with the results from a ~2000
670 mg digestion of NWA 5697 (-A) ($+0.039 \pm 0.001\text{‰}$, $n = 2$, 2SD) (Extended Data Fig. 3b). This
671 confirms that the analytical protocol utilised in this study is sufficient to destroy potential
672 fluorides formed from HF digestions.

673 ii) The robustness of the protocol to eliminate fluorides can be further tested by a second set of
674 experiments, where fractions (12-14%) of the NWA 530, NWA 1232, NWA 4428, and NWA
675 1563 digestions were spiked and heated within 6 M HCl on a hot plate whereas the remaining
676 solutions were spiked and placed into Parr Bomb with 14 M HNO₃ acids at 190 °C for a day.
677 All the four samples have identical $\delta^{49}\text{Ti}$ values between the two procedures within an
678 uncertainty of $\pm 0.010\text{‰}$ (Extended Data Fig. 3c).

679 As heterogeneity does exist inside chondrites, e.g., the large $\delta^{49}\text{Ti}$ variation of -4% to $+4\%$ in
680 Ca, Al-rich inclusions⁷¹, acquiring mass-dependent Ti isotope data for whole-rock chondrites
681 can be subject to a certain degree of such heterogeneity. This can be well corroborated by the
682 larger scatter in published $\delta^{49}\text{Ti}$ data for whole-rock chondrites with the decreasing digestion
683 masses (Extended Data Fig. 4). In this study, excluding Talbachat n'aït Isfoul (LL3) and NWA
684 2364 (CV3) that are likely subject to sample heterogeneity and show the elevated $\delta^{49}\text{Ti}$ values,
685 the remaining 22 chondrite samples define an average $\delta^{49}\text{Ti}$ of $+0.053 \pm 0.024\%$ (2SD) or \pm
686 0.005% (2SE) (Extended Data Fig. 4). Our new chondrite average is identical to that of Deng
687 et al.³⁴ ($+0.071 \pm 0.085\%$, $n = 22$, 2SD) and Williams et al.³⁵ ($+0.047 \pm 0.071\%$, $n = 6$, 2SD),
688 but with a 3-fold improvement in precision. Considering the large digestion masses for most
689 of the chondrite samples in this study, our new chondrite data should be least affected by
690 sample heterogeneity. The new chondrite average is resolved to be $\sim 0.052\%$ higher than that
691 of modern normal-type mid-ocean ridge basalts (N-MORBs), i.e., $+0.001 \pm 0.015\%$ (2SD) or
692 $\pm 0.004\%$ (2SE)(refs. 3,4) (Extended Data Fig. 4).

693 We note that data offset between laboratories also exists for the $\delta^{49}\text{Ti}$ results from Archean
694 komatiites, with the significantly lower and more scattered $\delta^{49}\text{Ti}$ values in Greber et al.³³ than
695 those in this study and Deng et al.⁴ (Extended Data Fig. 5). We emphasise that the presence of
696 data discrepancy between digestion duplicates of the same komatiite powders in Greber et al.³³
697 likely points to a larger analytical uncertainty on the reported $\delta^{49}\text{Ti}$ dataset for both whole-rock
698 chondrites and Archean komatiites than the claimed precision of $\pm 0.030\text{-}0.034\%$ (95% CI) for
699 individual samples.

700 *Quantifying mass exchange between mantle and crustal reservoirs in deep time*

701 Assuming that the continental crust (CC) at time t_i and the mantle equilibrated with the recycled
702 crustal melting residues from continental crust formation (thereafter called as the contaminated
703 mantle, i.e., CM), together form a primitive mantle (PM) reservoir with respect to TiO_2 content

704 and $\delta^{49}\text{Ti}$, the TiO_2 fraction from continental crust in the CC-CM combination at time t_i (i.e.,
 705 $X_{\text{TiO}_2\text{-CC}_t_i}$) should be:

$$706 \quad X_{\text{TiO}_2\text{-CC}_t_i} = \frac{C_{\text{TiO}_2\text{-CC}} \times q_{\text{CC}_t_i} \times m_{\text{CC}}}{C_{\text{TiO}_2\text{-PM}} \times (q_{\text{CC}_t_i} \times m_{\text{CC}} + m_{\text{CM}})}, \quad (13)$$

707 where C_{TiO_2} represents the TiO_2 content and m stands for the mass. We note that $q_{\text{CC}_t_i}$ defines
 708 the fraction of the total continental crust (m_{CC}) that has been produced until time t_i , which has
 709 been provided in the continental crust growth models from refs. 43 and 44. The Ti isotopic
 710 composition of the contaminated mantle (CM) at time t_i approximately should follow:

$$711 \quad \delta^{49}\text{Ti}_{\text{CM}_t_i} = \frac{\delta^{49}\text{Ti}_{\text{PM}} - \delta^{49}\text{Ti}_{\text{CC}} \times X_{\text{TiO}_2\text{-CC}_t_i}}{(1 - X_{\text{TiO}_2\text{-CC}_t_i})}, \quad (14)$$

712 Assigning $\delta^{49}\text{Ti}_{\text{PM}} = +0.053 \pm 0.005\%$ (this study) and the $\delta^{49}\text{Ti}$ average of Archean TTGs to
 713 be $\delta^{49}\text{Ti}_{\text{CC}} (+0.381 \pm 0.056\%$, 2SE, $n = 19$; this study and refs. 5 and 7), $\delta^{49}\text{Ti}_{\text{CM}_t_i}$ is controlled
 714 by $X_{\text{TiO}_2\text{-CC}_t_i}$. As $C_{\text{TiO}_2\text{-PM}}$ and $C_{\text{TiO}_2\text{-CC}}$ can be reasonably assumed to be 0.18 wt% and 0.34 wt%,
 715 respectively, $X_{\text{TiO}_2\text{-CC}_t_i}$ is further related with two free parameters, i.e., m_{CC} and m_{CM} in
 716 equation 13. Although modern continental crust is $\sim 0.55\%$ of the bulk silicate Earth (BSE) in
 717 mass (i.e., $m_{\text{CC}_\text{modern}} = 0.0055 \times m_{\text{BSE}}$), the total mass of continental crust (m_{CC}) ever
 718 produced throughout the Earth's history remains less clear. To quantify $\delta^{49}\text{Ti}_{\text{CM}_t_i}$, we can bring
 719 in two free parameters, i.e., k describing the total mass continental crust ever produced in the
 720 Earth's history after a normalisation to its modern mass ($k = m_{\text{CC}}/m_{\text{CC}_\text{modern}}$) and f represents
 721 the fraction of Earth's mantle to equilibrate with the recycled melting residues, i.e., $f =$
 722 $(m_{\text{CC}} + m_{\text{CM}})/m_{\text{BSE}}$. By assuming k and f , we can obtain the evolution of $\delta^{49}\text{Ti}_{\text{CM}}$ through time
 723 in Fig. 2 based on the continental crust growth models from refs. 43 and 44.

724 **Data Availability**

725 [All data are available at EarthChem⁷⁴](#). Data supporting the findings of this study are [provided](#)
 726 [with the paper](#) (including Methods and Extended Data).

727 References in **Methods** section

- 728 64. Jackson, M.G., Price, A.A., Blichert-Toft, J., Kurz, M.D., & Reinhard, A.A. Geochemistry
729 of lavas from the Caroline hotspot, Micronesia: Evidence for primitive and recycled
730 components in the mantle sources of lavas with moderately elevated $^3\text{He}/^4\text{He}$. *Chem. Geol.*
731 **455**, 385-400 (2017).
- 732 65. Hart, S.R. & Jackson, M.G. Ta'u and Ofu/Olosega volcanoes: The "Twin Sisters" of Samoa,
733 their P, T, X melting regime, and global implications. *Geochem. Geophys. Geosyst.* **15**.
734 (2014). DOI: 10.1002/2013GC005221
- 735 66. Workman, R.K. et al. Recycled metasomatized lithosphere as the origin of the Enriched
736 Mantle II (EM2) end-member: Evidence from the Samoan Volcanic Chain. *Geochem.*
737 *Geophys. Geosyst.* **5**. (2004). DOI: 10.1029/2003GC000623
- 738 67. Toplis, M.J. & Carroll, M.R. An experimental study of the influence of oxygen fugacity on
739 Fe-Ti oxide stability, phase relations, and mineral-melt equilibria in ferro-basaltic systems.
740 *Contrib. Mineral. Petrol.* **36**, 1137-1170 (1995).
- 741 68. Zhang, J., Dauphas, N., Davis, A.M. & Pourmand, A. A new method for MC-ICP-MS
742 measurement of titanium isotopic composition: Identification of correlated isotope
743 anomalies in meteorites. *J. Anal. At. Spectrom.* **26**, 2197-2205 (2011) .
- 744 69. Trinquier, A. et al. Origin of nucleosynthetic isotope heterogeneity in the solar
745 protoplanetary disk. *Science* **324**, 374-376 (2009) .
- 746 70. Zhang, J., Dauphas, N., Davis, A.M., Leya, I. & Fedkin A. The proto-Earth as a significant
747 source of lunar material. *Nature Geosci.* **5**, 251-255 (2012) .
- 748 71. Davis, A.M. et al. Titanium isotopes and rare earth patterns in CAIs: Evidence for thermal
749 processing and gas-dust decoupling in the protoplanetary disk. *Geochim. Cosmochim. Acta*
750 **221**, 275-295 (2018).

- 751 72. Rudge, J.F., Reynolds, B.C. & Bourdon B. The double spike toolbox. *Chem. Geol.* **265**,
752 420-431 (2009) .
- 753 73. Millet, M.A. & Dauphas, N. Ultra-precise titanium stable isotope measurements by double-
754 spike high resolution MC-ICP-MS. *J. Anal. At. Spectrom.* **29**, 1444-1458 (2014) .
- 755 74. Deng, Z. et al. Titanium stable isotopic compositions of chondrites and ancient to modern
756 terrestrial mantle-derived lavas. Version 1.0. Interdisciplinary Earth Data Alliance (IEDA)
757 <https://doi.org/10.26022/IEDA/112942> (2023).

758

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766 **Author Contributions**

767 Z.D., M.B. and M.S. conceived the idea and designed the project. Z.D., M.S., and L.P.
768 contributed to the methodology. Z.D., M.S., M.G.J. and M.B. selected the samples for study.
769 Z.D., K.N. and M.S. carried out the research and analysed the data. Z.D., M.S., M.G.J., M.A.M.,
770 L.P., K.N., N.S.S., D.H., and M.B. participated into interpreting the data. Z.D., M.B., M.S. and
771 L.P. wrote the manuscript with inputs from all the co-authors.

772 **Author Information**

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774 declares no competing financial interests. Readers are welcome to comment on the online

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777 **Extended data and captions**

778 **Extended Data Table 1** Titanium isotope results of terrestrial rock standards.

779 **Extended Data Table 2** Results of experiments on whole-rock chondrites.

780 **Extended Data Table 3** Titanium isotopic results of whole-rock chondrites.

781 **Extended Data Table 4** Chemical and Ti isotopic data of Archean to Proterozoic samples from
782 this study and literature.

783 **Extended Data Table 5** Chemical, Sr, and Ti isotopic data of modern oceanic island basalts
784 (OIBs) and mid-ocean ridge basalts (MORBs).

785 **Extended Data Figure 1 Chemical and isotopic data of the mantle-derived samples from**
786 **this study. (a)** Strontium and neodymium isotope data of the studied modern oceanic island
787 basalt (OIB) samples. The mantle end members and global OIB data are adapted from White
788 et al.⁴⁶. **(b)** Plot of $\delta^{49}\text{Ti}$ versus MgO for the studied mantle-derived rocks. Note that MgO
789 contents of the studied ~ 3.5 Ga Barberton komatiites and those of basaltic komatiites are
790 assumed to be 20 wt% and 10 wt%, respectively.

791 **Extended Data Figure 2 Comparing the measured ^{50}Ti anomalies of bulk chondrites and**
792 **terrestrial rocks with those from literature.** Chondrite samples Murchison, Orgueil, SaH
793 97159 and NWA 5697 are plotted basing on the reasonings that: i) enstatite chondrites (e.g.,
794 SaH 97159), Murchison, and Orgueil were previously shown to have small variations in ^{50}Ti
795 anomaly among various digestion aliquots, therefore being suited to check the robustness of
796 ^{50}Ti measurements in this study; and ii) NWA 5697 in this study was digested with a large
797 mass of powders (~ 2 g), which should not be affected much by heterogeneity inside the sample.
798 The $\epsilon^{50}\text{Ti}$ values of SaH 97159 and NWA 5697 are comparing to the mean values of the
799 literature data for enstatite chondrites and ordinary chondrites^{69,70}, respectively.

800 **Extended Data Figure 3 Comparing duplicate measurement results from this study with**
801 **those from literature. (a)** Duplicate measurement results of komatiite and eucrite samples in

802 Greber et al.³³ (b-c) Experiments on whole-rock chondrites that involve two different spiking
803 procedures: NWA 5697, NWA 530, NWA 1232, NWA 4428, and NWA 1563. Our analytical
804 procedure has improved the data reproducibility by 3- to 5-fold relative to those reported in
805 Greber et al.³³ (a).

806 **Extended Data Figure 4 Comparing the $\delta^{49}\text{Ti}$ data of whole-rock chondrites from this**
807 **study and literature with the digestion masses.** The typical digestion masses for individual
808 chondrite samples are ~50-100 mg in Greber et al.³³, 5.3-35 mg in Deng et al.³⁴ and ≥ 100 mg
809 in Williams et al.³⁵. The method in this study has improved the measurements of $\delta^{49}\text{Ti}$ values
810 for whole-rock chondrites by 3-fold, comparing to the previous data from ref. 33 (the triangles),
811 ref. 34 (the diamonds) and ref. 35 (the circles). [The depleted MORB mantle value from refs. 3](#)
812 [and 4 is shown for comparison.](#)

813 **Extended Data Figure 5 Comparing the $\delta^{49}\text{Ti}$ data of Archean mantle-derived rocks from this**
814 **study (the orange circles), ref. 4 (the light orange circles) and ref. 33 (the white circles).** The
815 $\delta^{49}\text{Ti}$ averages of whole-rock chondrites from this study and the N-MORB samples from refs.
816 3 and 4 are also shown for comparison.

817