

Marine Geology

Sr isotope variations in Oligocene–Miocene and modern biogenic carbonate formations of Koko Guyot (Emperor Seamount Chain, Pacific Ocean)

--Manuscript Draft--

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Abstract:	<p>The Hawaiian–Emperor Seamount Chain, a major topographic feature of the Pacific Ocean floor, is composed of seamounts capped with fossil coral reef deposits that originally formed close to sea level but are now covered by hundreds of meters of water owing to prolonged subsidence. These fossil reef deposits are important archives of paleoenvironmental change and yield information on the subsidence history of the seamounts. We studied the Sr isotope compositions of Oligocene–Miocene coral reef limestone from Koko Guyot in the southern Emperor Seamount Chain to assess the dynamics of the subsidence. The ages of the studied samples containing coral fragments established by Sr isotope stratigraphy vary from 26.3 to 20.1 Ma. In contrast, the youngest samples (15.3 Ma), which were deposited in water depths of >120 m, are barren of corals and are composed exclusively of bryozoans and coralline algae. The subsidence rate of the Koko Guyot volcanic structure was not constant over time. Integration of our new data with the results of previous studies reveals that the subsidence rate was 0.046 ± 0.005 mm/yr during the first 25–30 Myr (from 49–44 to 20 Ma). During this period, Koko Guyot was in a bathymetric interval favorable for coral reef development, and its subsidence was compensated by rapid vertical growth of the reef. Subsequently, the subsidence rate decreased to an average value of 0.019 ± 0.003 mm/yr from 20 to 15 Ma. The decrease in the rate of bottom subsidence coincided with unfavorable environmental conditions for coral reef development, leading to the disappearance of corals. The average subsidence rate has been 0.015 ± 0.002 mm/yr since 15 Ma, comparable to the present-day subsidence rate. We also analyzed the stable Sr isotope ratios ($\delta^{88}\text{Sr}/86\text{Sr}$) of warm-water coral samples formed at 25–20 Ma ($0.32\text{‰} \pm 0.1\text{‰}$), as well as carbonate of large benthic foraminifera, coralline algae, and other non-coral species for the period 20–15 Ma ($0.10\text{‰} \pm 0.09\text{‰}$). We suggest that the large difference in carbonate $\delta^{88}\text{Sr}/86\text{Sr}$ between 25–20 and 20–15 Ma corresponds to a difference in the fractionation factor caused by environmental and benthic community change.</p>
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<p>Response to Reviewers:</p>	

Dear Editor and Reviewer,

Thank you very much for your review of our manuscript titled "Sr isotope variations in Oligocene–Miocene and modern biogenic carbonate formations of Koko Guyot (Emperor Seamount Chain, Pacific Ocean)". We have revised our article and would like to present it to you.

Some comments had incorrect line numbers. We found what they referred to and signed the correct line numbers in the answers.

We submitted the text for professional proofreading to Stallard Scientific Editing, where we corrected the entire text. We left the grammatical and punctuation corrections in the file with marks. Following their recommendations, we improved the understanding of Fig. 1, 4, 5, 6 and tables 1 and 2.

Also, throughout the text we have changed "biocommunity" to "benthic community" because this is more paleontological correct.

Below are the responses to your comments.

Response to the Reviewer #1's comments:

Line 47-52 - Suggested revision: "We also analyzed the stable Sr isotope ratios ($d_{88/86}\text{Sr}$) of warm-water coral samples formed 25-20 Ma ago ($0.32 \pm 0.1\text{‰}$) and more recent carbonate composed of Larger benthic foraminifera, and coralline algal, and other non-coral species from 20-15 Ma ($0.10 \pm 0.09\text{‰}$). We suggest that the large difference in carbonate $d_{88/86}\text{Sr}$ between these two intervals corresponds to a difference in fractionation factor due to environmental and biocommunity change." - **corrected**

Line 73 - Moving the geological background information for Koko Guyot to the following section was helpful for readability, but you need to check that the necessary introductory information is still provided here (specifically, you do not transition from discussing the Emperor Seamount Chain generally to your description of reef growth on Koko Guyot). Add a condensed description of Koko Guyot here before you begin referring to it specifically in Line 96. – **corrected**.

Line 120 - Good additional description of novelty (new sampling method); in 122-124, I suggest rephrasing to: "Our purpose was to confirm the previous estimates by Clague et al. (2010) with samples taken from a site remote from the area of previous work and, if possible, improve them by...." (Explain specifically how they could be improved; reducing uncertainty?). – **corrected in lines 98-101**

Line 139 -169 - Check organization of these paragraphs now that you have moved information from the introduction to this section; you refer to Koko Guyot in the first paragraph, and then reintroduce it in the second. Rewrite to avoid redundancy. **Lines 120-143**

Line 224 - Clarify: other studies have used both TIMS and MC-ICP-MS to measure stable Sr. Here it initially sounds as though you used both methods in this study. "... have been measured in other studies using both..." – **corrected in line 197**

Line 309 - Clarify: The ratio of $^{88}\text{Sr}/^{86}\text{Sr}$ in carbonates depends on the $^{88}\text{Sr}/^{86}\text{Sr}$ ratio of seawater, which changes through time due to variation in the same fluxes that control seawater $^{87}/^{86}$ as well as the net carbonate flux from the ocean, and the degree of fractionation between seawater and carbonate, which depends on species and

temperature. This is important to distinguish because when you compare your data to the Paytan et al. 2021 curve, it is the offset between the seawater curve and your data that may tell you something about changes in species/environment (that is, I would not necessarily expect your carbonate values to line up with the seawater values but rather be offset by some constant (or variable) fractionation factor). - **corrected in line 277**

Line 313- Rephrase: "Minerals like carbonate formed in seawater are generally characterized by lower $d_{88/86}\text{Sr}$ because of seawater-mineral fractionation. Moreover, minerals of chemogenic and biogenic origins can be distinguished by the degree of their stable Sr isotope fractionation (Fietzke and Eisenhauer, 2006; Fruchter et al., 2016) which may depend on temperature and varies for different species. Thus..." **corrected in lines 280-283**

Line 324 - Without a conceptual framework for the direction of change you expect to see, the stable Sr data is not all that useful for inferring anything about the nature of the species transition or environmental shift. I do think that your revisions somewhat (rightly) de-emphasized the use of stable Sr isotopes as a diagnostic tool for environmental change in this setting. Rather, you have generally tested the idea that a community shift you have independently inferred (i.e., reef assemblages replaced by cold water species) might have an impact on stable Sr isotopes (because of the known dependencies of the seawater-carbonate fractionation factor on species and temperature that you introduce above). I suggest that you rewrite Line 324-325 to explain that within the scope of this study, you are looking to see if $d_{88/86}\text{Sr}$ of your specific samples shift in relation to the subsidence and migration of the guyot and subsequent environmental changes, but in this case the $d_{88/86}\text{Sr}$ measurements do not provide an independent proxy for these changes and there are many factors that complicate their interpretation. **corrected in lines 290-292**

Line 357 - Rephrase: "Because secondary processes have been shown to alter the initial $d_{88/86}\text{Sr}$ of carbonates, we use only the three samples that are the least modified in our discussion." **corrected in lines 318-320**

Line 361 - Specify what the agreement between the carbonate samples $d_{88/86}\text{Sr}$ and seawater curve indicates (these particular carbonate samples apparently fractionated very little from seawater?). It is important to note that you don't necessarily expect the carbonate values to line up with the seawater values, and then explain why these might. Add explanations to address these questions: The error bar is quite large, but is it possible that these have in fact undergone some alteration (would this lead to increased $d_{88/86}\text{Sr}$ values relative to initial composition)? Is there evidence in the literature that the assemblages you expect to be represented by these samples would fractionate $<0.09\%$ from seawater? Are these non-representative samples, possibly explaining why Lv86-9-6 is slightly different (though within error) compared to the other two? You should more thoroughly present the possible complications here. - **corrected in line 321,**

Line 369 - Specify that in the absence of significant changes in seawater $d_{88/86}\text{Sr}$, the dramatic difference between carbonate and seawater in this interval likely indicates larger fractionation between seawater and carbonate compared to the earlier interval. Then you can hypothesize what might be driving this fractionation. **corrected in line 323.**

Line 371 - Start new paragraph and revise for clarity: "Biocommunity alteration to much more cool water resistance can be correlated with the bottom subsidence rate and guyot migration to higher latitudes (Wilson, 1963; Clague and Dalrymple, 1987; Tarduno

et al., 2003; Clague et al., 2010). The change in the temperature and light regime as Koko Guyot subsided and migrated led to biocommunity alteration as reef benthic assemblages were replaced as the dominant species by larger foraminiferal species. We suppose that this biocommunity transition is expressed in the dramatic decrease of $\delta^{88}/^{86}\text{Sr}$ in our samples (Fig. 4) in the absence of major changes in seawater $\delta^{88}/^{86}\text{Sr}$." **corrected in lines 324-329.**

Line 377 - Move sentence about modern echinoid $\delta^{88}/^{86}\text{Sr}$ values to Line 371 before new paragraph and add comparison of the fractionation between seawater-echinoid today vs. seawater-carbonate from 20 to 15 Ma. **corrected in line 330.**

Line 378 - I don't think you have enough information to draw this broad conclusion. Rather, you can simply say that you observe a shift in the $\delta^{88}/^{86}\text{Sr}$ of your samples that seems to coincide with the biocommunity transition, suggesting the fractionation factor possibly changed along with environmental factors (temperature, dominant species) as might generally be expected. However, complicating factors (be specific) limit further interpretation of these data. **corrected in line 331.**

Line 447 - See Line 378 comment above and revise. - **corrected in lines 398-401.**

Line 461 - In your introduction, you note that you hoped to improve the prior estimates. Summarize the specific advance and how these new rates fit into the overall picture of Pacific subsidence. That is, tell us specifically how "The data obtained refine the existing models of subsidence of the Pacific crust." - **corrected in lines 412-413.**

We would like to thank Editor-in-Chief of Marine Geology Dr. Adina Paytan and anonymous reviewers for their thorough comments and suggestions, which have improved our manuscript.

Sincerely yours,

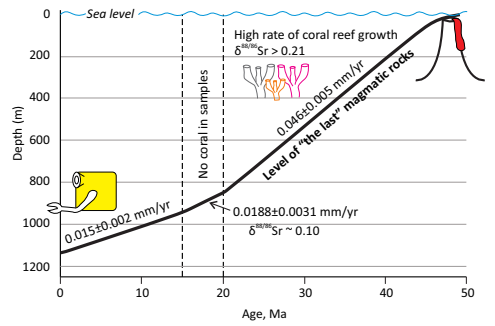
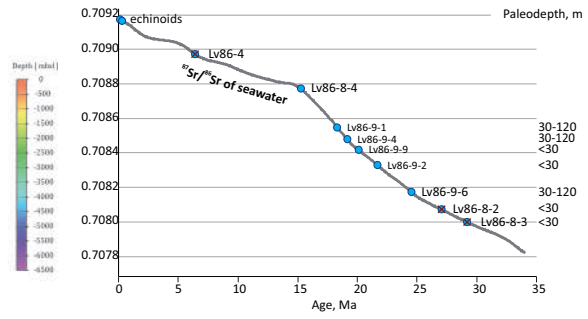
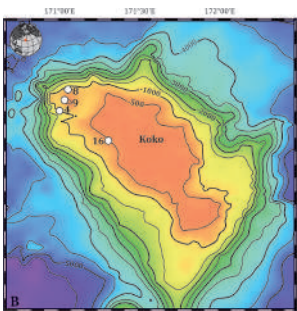
Irina Vishnevskaya

Highlights for paper Vishnevskaya et al., “Sr isotope variations ...”

The subsidence rate of Koko Guyot was not uniform

The age of corals and larger foraminiferal species was determined by strontium isotope stratigraphy.

The study of strontium isotope composition showed that the least altered limestones containing the fragments of reef corals were formed in the early Miocene



1 Sr isotope variations in Oligocene–Miocene and modern biogenic carbonate
2 formations of Koko Guyot (Emperor Seamount Chain, Pacific Ocean)

3

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26

27 ABSTRACT

28

29 The Hawaiian–Emperor Seamount Chain, a major topographic feature of the Pacific Ocean floor,
30 is composed of seamounts capped with fossil coral reef deposits that originally formed close to
31 sea level but are now covered by hundreds of meters of water owing to prolonged subsidence.
32 These fossil reef deposits are important archives of paleoenvironmental change and yield
33 information on the subsidence history of the seamounts. We studied the Sr isotope compositions
34 of Oligocene–Miocene coral reef limestone from Koko Guyot in the southern Emperor

35 Seamount Chain to assess the dynamics of the subsidence. The ages of the studied samples
36 containing coral fragments established by Sr isotope stratigraphy vary from 26.3 to 20.1 Ma. In
37 contrast, the youngest samples (15.3 Ma), which were deposited in water depths of >120 m, are
38 barren of corals and are composed exclusively of bryozoans and coralline algae. The subsidence
39 rate of the Koko Guyot volcanic structure was not constant over time. Integration of our new
40 data with the results of previous studies reveals that the subsidence rate was 0.046 ± 0.005
41 mm/yr during the first 25–30 Myr (from 49–44 to 20 Ma). During this period, Koko Guyot was
42 in a bathymetric interval favorable for coral reef development, and its subsidence was
43 compensated by rapid vertical growth of the reef. Subsequently, the subsidence rate decreased to
44 an average value of 0.019 ± 0.003 mm/yr from 20 to 15 Ma. The decrease in the rate of bottom
45 subsidence coincided with unfavorable environmental conditions for coral reef development,
46 leading to the disappearance of corals. The average subsidence rate has been 0.015 ± 0.002
47 mm/yr since 15 Ma, comparable to the present-day subsidence rate. We also analyzed the stable
48 Sr isotope ratios ($\delta^{88/86}\text{Sr}$) of warm-water coral samples formed at 25–20 Ma ($0.32\% \pm 0.1\%$), as
49 well as carbonate of large benthic foraminifera, coralline algae, and other non-coral species for
50 the period 20–15 Ma ($0.10\% \pm 0.09\%$). We suggest that the large difference in carbonate
51 $\delta^{88/86}\text{Sr}$ between 25–20 and 20–15 Ma corresponds to a difference in the fractionation factor
52 caused by environmental and benthic community change.

53

54 *Key words:*

55 $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, $\delta^{88/86}\text{Sr}$, Corals, Bryozoans, Larger foraminifera, Subsidence, Hawaiian–Emperor
56 Seamount Chain, Hawaiian hotspot

57

58 **1. Introduction**

59

60 The Emperor Seamount Chain (Pacific Ocean) includes more than a dozen seamounts
61 (i.e., extinct volcanoes). The northernmost seamount of Meiji is considered the oldest, with an
62 age estimated at 85 Ma (Keller et al., 2000). The youngest seamount of Daikakuji (42 Ma;
63 Dalrymple and Clague, 1976) is located at the junction of the Emperor Seamount Chain with the
64 Hawaiian Seamount Chain (Fig. 1). Koko Guyot is the southernmost seamount and one of the
65 largest in the Emperor Seamount Chain, with a surface area of 5800 km² (Greene et al., 1980).
66 This guyot is located from 34°N to 36.5°N and from 170.8°E to 171.5°E. The top of the guyot is
67 positioned at a minimum depth of 270 m below sea level (Matter, Gardner, 1975) and is
68 characterized by a predominantly flat upper surface at 300–400 m water depth.

69 The Emperor–Hawaiian Seamount Chain formed as a result of the prolonged activity of
70 the so-called Hawaiian hotspot, a long-lived mantle plume beneath the Pacific Plate (Jackson et
71 al., 1980; Clague and Dalrymple, 1987; Tarduno et al., 2003; and references therein). Plate
72 movement relative to conventionally stationary mantle structure led to the formation of a linear
73 chain of volcanic islands and seamounts with ages increasing from south to north. The
74 seamounts situated in the southern Emperor Seamount Chain are topped with a sediment cover
75 containing carbonate rocks (Shipboard Scientific Party, 1975a, 1975b, 2002), which represent an
76 excellent record of geochemical, paleontological, and paleogeographic settings.

77 The following development sequence for seamounts has been established (Wheeler and
78 Aharon, 1991). After the cessation of volcanic activity, a coral reef began to develop on the
79 volcanic island. Over time, the volcano subsided, and the coral reef at first kept pace with
80 relative sea-level rise by enlarging upward. As the oceanic crust moved away from the area of
81 plume activity and cooled, the volcano subsided further, and the coral reef (which was unable to
82 keep up with sea-level rise) drowned. Although the main cause of the demise of the coral was the
83 rapid relative sea-level rise, other factors such as a decrease in sea surface temperature as the
84 volcanic island migrated to higher latitudes by plate motion may also have been influential (e.g.,
85 Clague et al., 2010).

86 Data regarding the speed and direction of movement of the Hawaiian hotspot and the
87 Pacific Plate show that the paths of Koko Guyot and the hotspot diverged (*c.* 45 Ma), whereby
88 the seamount moved to the north and the hotspot moved to the south (Wilson, 1963; Clague and
89 Dalrymple, 1987; Tarduno et al., 2003). Clague et al. (2010) studied corals in southern Koko
90 Guyot and used Sr isotope stratigraphy to date the carbonates. According to those authors’
91 calculations, Koko Guyot migrated northward at a rate of 69 km/Myr during the first 5 Myr (*c.*
92 50–45 Ma) of its existence, moving from 21.5° to 23°N. In addition, the rate at which the guyot
93 migrated decreased to 31 km/Myr between 45 Ma and the present, and the direction of
94 movement changed to the northwest before reaching its present position at 35°N. Clague et al.
95 (2010) proposed a two-phase subsidence history for Koko Guyot: (1) ~0.009 mm/yr from 27.1 to
96 16.2 Ma; and (2) ~0.014 mm/yr from 16.2 Ma to the present. Those authors also suggested that
97 the timing of reef growth cessation at Koko Guyot occurred at *c.* 29 Ma, on the basis of the
98 youngest age of sampled corals (27 Ma) and the calculated average subsidence rate (0.012
99 mm/yr).

100 We studied samples obtained from the northwestern part of Koko Guyot, where sampling
101 has hitherto not been conducted. We used a new sampling method for this region, namely, a
102 remotely controlled underwater vehicle (see “Material and Methods”), so our samples could be
103 geographically and bathymetrically referenced. Our purpose was to confirm the previous

104 estimates of coral age and subsidence rate made by Clague et al. (2010) with samples taken from
105 a site distant from the area of previous work and, if possible, improve the estimates by measuring
106 isotope ratios using a different type of equipment (a Neptune Plus multicollector inductively
107 coupled plasma mass spectrometry (ICP–MS) instrument versus a VG Sector 54 Thermal
108 ionization mass spectrometer (TIMS) in Clague et al. (2010)) and reducing uncertainties in age
109 estimates. The aim of the study was to establish the youngest age limit of coral reefs on Koko
110 Guyot and further constrain the timing of coral reef drowning as Koko Guyot became
111 submerged. In addition, to improve the understanding of the subsidence history of Koko Guyot,
112 we used differences in the ages of sampled corals and their depths to calculate the average
113 subsidence rate of this volcanic structure for different periods. To achieve these aims, we
114 performed paleontological analysis and measured the Sr isotope compositions of samples
115 collected from the Koko Guyot. We compared the obtained $^{87}\text{Sr}/^{86}\text{Sr}$ ratios with the variation
116 curve of this ratio for the Cenozoic (McArthur et al., 2001, 2020). In addition, we used the
117 $\delta^{88/86}\text{Sr}$ record measured in carbonates as a proxy for environmental change on the flooded reef
118 platform.

119

120 **2. Materials and methods**

121

122 The 86th voyage of the research vessel “Akademik M.A. Lavrentiev” was held during
123 July–August 2019. The aim of the expedition was to conduct a comprehensive study of the
124 seamounts of the southern Emperor Seamount Chain. The subject of the present study, the
125 southernmost and youngest seamount of the Emperor Seamount Chain (i.e., Koko Guyot), is an
126 isolated underwater volcanic seamount with a flat top lying more than 300 m below present
127 mean sea level. The guyot is composed mainly of alkaline basalts with minor tholeiitic basalts
128 (Clague and Dalrymple, 1987). The final stage of eruptions is represented by interlayered
129 pahoehoe flows, subaerial aa units, and flow foot breccias. During the course of previous studies
130 as part of the Deep Sea Drilling Program (DSDP) and Ocean Drilling Program (ODP), several
131 sediment cores were recovered: DSDP Leg 32 sites 308 and 309 (Shipboard Scientific Party,
132 1975a, 1975b) and ODP Leg 197 Site 1206 (Shipboard Scientific Party, 2002). The materials
133 collected during those expeditions allowed the earliest sedimentation stages and waning of
134 volcanic activity to be investigated, as well as fossil benthic assemblages, paleoenvironmental
135 setting, and ages volcanic and sedimentary rocks. At ODP Site 1206, lava flows are separated by
136 limestone and volcanoclastic sandstone layers (Tarduno et al., 2003), suggesting the near-surface
137 nature of the eruptions. The age of the volcanic edifice of the Koko Guyot is estimated as 49–48
138 Ma (Jackson et al., 1980; Tarduno et al., 2003; Duncan and Keller, 2004). The minimum age of

139 the Koko eruptions has been determined from nannofossils occurring at the base of the
140 sedimentary cover, which probably overlaps the last lava flow, and coincides with biozones
141 NP14 and NP15 (middle Eocene; Speijer et al., 2020). A seismic survey of the Koko Guyot has
142 shown that the volcanic structure is covered by a ~600-m-thick carbonate cap associated with
143 coral reef deposits (Davies et al., 1972). The exposed sedimentary part of drill cores from DSDP
144 sites 308 and 309 is composed of altered volcanoclastic siltstones and sandstones with a sharp
145 contact between them. The sandstones contain bioclasts of bryozoans, solitary corals, ostracods,
146 coralline algae, benthic foraminifera, mollusks, and ooids. The fossil assemblage indicates an
147 early Eocene shallow-water setting (Larson et al., 1975).

148 The materials collected for the present study were collected using a remotely operated
149 underwater vehicle (Comanche, SUB-Atlantic, UK), equipped with Schilling Robotics Orion
150 hydraulic manipulators, and a Sonardyne hydroacoustic positioning system coupled with a GPS
151 navigation system. During the voyage, 11 dives were performed to survey the top and slopes of
152 Koko Guyot. Carbonate material was collected during four dives, three of which were performed
153 on the northwestern peak of the guyot (dives 4, 8, and 9; Fig. 1) and the fourth in the western
154 part of the main plateau (dive 16; Fig. 1). A living deep-sea isidid octocoral, also termed
155 “bamboo coral”, was collected during dive 4. We used this octocoral as a reference for modern
156 carbonate accumulation. Sampling points and physical water characteristics are presented in Fig.
157 1 and Table 1. Carbonate rocks were collected directly with a manipulator operated from the
158 surface (Fig. 2A) and with a 15 cm × 15 cm scoop net (Fig. 2B). For rocks collected by the
159 manipulator, a block measuring 1.5 cm × 1.5 cm × 1.5 cm in size was cut from the central part of
160 each rock sample. These cubes were passed through a magnet to remove any metal shavings
161 from the saw and washed in distilled water. For material collected by the scoop net, the sediment
162 was washed with seawater and sorted into different grain-size fractions from 1 to 50 mm. After
163 careful visual inspection, the lightest-colored and unaltered samples devoid of Fe–Mn oxide–
164 hydroxide coatings were selected for geochemical analyses. The selected samples were washed
165 with a brush in running water and finally rinsed in distilled water. All samples were
166 photographed directly on board.

167 Further sample preparation was carried out in the cleanrooms (class 1000) and laminar
168 boxes (class 100) of the Laboratory of Physical and Chemical Methods of Analysis, Zavaritsky
169 Institute of Geology and Geochemistry UB RAS, Ekaterinburg, Russia. Fragments of carbonate
170 rocks without an outer crust and individual parts of fossils weighing about 100 mg were washed
171 three times in ultrapure water (AriumPro, Sartorius). Then, 5 ml of 1N HCl were added.
172 Although complete dissolution of all the material occurred during the first few minutes, the
173 samples were left in the acid for 24 h at room temperature. The solution was then centrifuged for

174 20 min at 6000 rpm in an EBA 21 centrifuge (Hettich, Germany). The resulting supernatant was
175 taken from the central part of the liquid column so that undissolved residue containing the flakes
176 of possible organic matter would not enter the resulting liquid. Measurements showed that Fe
177 and Mn contents were less than 50 ppm and less than 20 ppm in the majority of the samples,
178 respectively. These values are consistent with data for the lattice phases of foraminiferal calcite
179 from Palmer (1985) and provide evidence for the lack of secondary Fe–Mn oxide–hydroxides in
180 the studied solutions. The resulting liquid was divided into two aliquots: 2 ml was transferred to
181 test tubes for elemental analysis, and the rest of the liquid was retained for Sr isotope analysis.

182 An ICP–atomic emission spectrometry (AES) instrument (Optima-8000 DV,
183 PerkinElmer, USA) was used to determine major-element compositions, including Mg, Mn, Sr,
184 and Al, as well as traces of Fe. Control of the accuracy and precision of major- and trace-element
185 compositions was performed using IAG/CGL 020 ML-3 certified limestone provided by the
186 Central Geological Laboratory of Mongolia. The contents of major and trace elements were
187 measured on a regular basis during 2019, yielding the following contents: Fe = 2350 ± 350 ppm,
188 Al = 6000 ± 900 ppm, Mn = 180 ± 30 ppm, Mg = 8400 ± 1260 ppm, and Sr = 1000 ± 150 ppm
189 (2SD, N = 30). The obtained contents were in good agreement with the certified values of Fe =
190 2400 ± 100 ppm, Al = 6100 ± 100 ppm, Mn = 178 ± 8 ppm, Mg = 8350 ± 145 ppm, and Sr =
191 1018 ± 30 ppm (Certificate of analysis IAG / CGL 020 ML-3 (Limestone), 2015). The precision of
192 each individual result (relative standard deviation or RSD) was better than 1%.

193 The volumes of liquid samples calculated to match ~300 ppb of Sr were placed in a PFA
194 vial and evaporated to dryness on a hotplate at 120 °C. The residue was dissolved in 0.5 mL of
195 7M HNO₃, placed in an Eppendorf microtube, and centrifuged at 6000 rpm for 15 min by an
196 EBA 21 centrifuge (Hettich, Germany). A single-step chromatography technique using SR-Resin
197 (100–200 mesh, Triskem®, TrisKem International, France) was applied for Sr isolation
198 (Vishnevskaya et al., 2020). Purified Sr fraction was evaporated to dryness and dissolved with
199 3% HNO₃ (v/v) for further isotope ratio measurement.

200 Stable Sr isotopic compositions have been measured in other studies using both TIMS
201 and MC–ICP–MS (McArthur et al., 2020; Teng et al., 2017). The double-spike (DS) technique is
202 usually applied for TIMS (Krabbenhöft et al., 2009; Shalev et al., 2013; Paytan et al., 2021) and
203 MC–ICP–MS (Shalev et al., 2013), although MC–ICP–MS analytical protocols have tended to
204 adopt standard-sample bracketing (SSB)–MC–ICP–MS (Fietzke and Eisenhauer, 2006; Moynier
205 et al., 2010; Charlier et al., 2012; Ma et al., 2013). In general, DS–TIMS is considered to have
206 the highest precision and accuracy, followed by DS–MC–ICP–MS and SSB–MC–ICP–MS.

207 Radiogenic and stable Sr isotopes were measured in this study using an MC–ICP–MS
208 Neptune Plus instrument (Thermo Fisher Scientific, Germany). The mass bias was corrected

209 using a combination of exponential law normalization ($^{87}\text{Sr}/^{86}\text{Sr} = 8.37861$) and bracketing, with
210 the normalized values being additionally corrected by the mean reference value of 0.710245 for
211 SRM-987 strontium carbonate (GeoReM database, <http://georem.mpch-mainz.gwdg.de/>). To
212 monitor the analytical procedure, SRM-987 was measured on a regular basis, yielding $^{87}\text{Sr}/^{86}\text{Sr} =$
213 0.710261 ± 0.000020 (2SD, N = 257). The precision of the determinations estimated as the
214 within-laboratory standard uncertainty (2σ) obtained for SRM-987 was $\pm 0.003\%$. The precision
215 of each individual result (1σ) during the sample measurement was better than ± 20 ppm. Long-
216 term analyses of $\delta^{88/86}\text{Sr}$ in SRM-987 processed through chromatographic columns and measured
217 as unknowns yielded $-0.01\% \pm 0.09\%$ (2SD, N = 34). In addition, NIST SRM 1400 bone ash
218 was analyzed as $\delta^{88/86}\text{Sr} = -0.33\% \pm 0.09\%$ (2SD, N = 10), in agreement with the value
219 provided in the GeoReM database. The precision of each individual result (1σ) was better than
220 $\pm 0.006\%$.

221

222 3. Results

223

224 The studied samples are composed of limestone with a fine-grained matrix (micrite)
225 containing abundant biogenic components (corals, coralline algae, molluscs, and benthic
226 foraminifera) and undetermined carbonate fragments. Several samples contain fossil corals,
227 including *Astrea cf. annuligera* Milne Edwards & Haime, 1849, *Porites* sp., and at least one
228 other undetermined Merulinidae (Table 2 and Fig. 3). Large benthic foraminifera (LBF)
229 represented by *Spiroclypeus tidoenganensis* Van der Vlerk, 1925 and *Heterostegina cf.*
230 *assilinoidea* (Blanckenhorn) Henson, 1937 occur in samples Lv86-9-6, Lv86-9-2, and Lv86-9-9
231 (sample numbers are given from oldest to youngest). Samples LV86-9 and LV86-16 consist of
232 cidaroid echinoderm spines (identified by Dr. K.V. Minin, Shirshov Institute of Oceanology of
233 Russian Academy of Sciences; Fig. 3B). The studied samples have a good degree of
234 preservation, as assessed by optical examination.

235 In general, under the influence of post-sedimentary fluids, Fe and Mn contents increase
236 and Sr and Mg decrease in carbonates (Veiser, 1983; Banner, 2004; Sawaki et al., 2010).
237 Consequently, by studying the mutual correlations of these elements, it is possible to identify
238 samples that have been least affected by diagenetic alteration. Samples with low Mn/Sr and
239 Fe/Sr ratios are interpreted as not having undergone diagenetic processes, meaning that their
240 isotope characteristics faithfully record those of the primary materials. The contents of Fe, Mn,
241 Al, Sr, and Mg in our samples are very low, except in three samples (Table 3). The Fe/Sr ratio is
242 particularly high in samples LV86-4 and LV86-8-2, with values of 0.74 and 0.77, respectively
243 (Table 3). Sample LV86-8-2 also has a high Mn/Sr ratio (0.37), as does LV86-8-3 (0.60). These

244 three samples (LV86-4, LV86-8-2, and LV86-8-3), for which at least one of the two ratios
245 (Mn/Sr and Fe/Sr) is high, are used with caution in our interpretations, and the isotopic data
246 derived from them are considered less reliable compared with other samples.

247 The Sr isotope compositions of two calcified echinoderm spines are very similar
248 ($^{87}\text{Sr}/^{86}\text{Sr} = 0.70917 \pm 0.000008$, $\delta^{88/86}\text{Sr} 0.24 \pm 0.01\%$). Samples LV86-4, LV86-8-2, and
249 LV86-8-3, which we infer to have undergone a degree of diagenetic alteration, have $^{87}\text{Sr}/^{86}\text{Sr}$
250 ratios of 0.708961, 0.708064, and 0.708000, respectively. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the remaining
251 limestones range from 0.70817 to 0.70877, with a mean value of 0.70845 (Table 4), and their
252 $\delta^{88/86}\text{Sr}$ values vary from 0.09‰ to 0.37‰, with a mean value of 0.22‰. An inverse relationship
253 is observed between $\delta^{88/86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ (correlation coefficient, $C_{\text{cor}} = -0.69$, $\rho = 0.13$),
254 meaning that $\delta^{88/86}\text{Sr}$ decreases with decreasing Sr isotopic age. There is a positive relationship
255 between isotopic composition and Sr content ($C_{\text{cor}} = 0.75$, $\rho = 0.08$). Here and below, the
256 correlation coefficient is calculated as

$$\text{Correl}(X, Y) = \frac{\sum (x - \bar{x})(y - \bar{y})}{\sqrt{\sum (x - \bar{x})^2 \sum (y - \bar{y})^2}}$$

257
258 where \bar{x} and \bar{y} are mean values of two arrays.

259

260 4. Discussion

261

262 4.1. Sr isotope composition: $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{88/86}\text{Sr}$

263

264 The Sr isotope composition of seawater is recorded at the time of formation of carbonate
265 skeletons of marine organisms (McArthur et al., 2001; Banner, 2004). The Sr isotope
266 composition of ocean water results from the mixing of several Sr sources with different isotopic
267 signatures (McArthur et al., 2001; Banner, 2004). Terrigenous material of continental origin with
268 high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (modern value of continental runoff of 0.7116; Palmer and Edmond, 1989)
269 is carried into ocean basins by rivers, glaciers, and wind. During the weathering of mid-ocean
270 ridge basalts and halmyrolysis of ocean-floor rocks, Sr with a low $^{87}\text{Sr}/^{86}\text{Sr}$ ratio enters the water
271 (modern value of 0.7037; Palmer and Edmond, 1989). The smallest sources of Sr are marine
272 carbonates, which release upon recrystallization a part of the Sr held in the crystal lattice, which
273 has an average isotopic ratio of 0.7084 (Holland, 1984; De Paolo, 1987; Davis et al., 2003;
274 Banner, 2004). The modern global-ocean $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is 0.70917 (Burke et al., 1982; Faure,
275 1986; Hodell et al., 1989; Banner, 2004; McArthur et al., 2012, 2020).

276 A comparison of the Sr isotope composition of carbonate rocks with the LOWESS global
277 $^{87}\text{Sr}/^{86}\text{Sr}$ variation curve (McArthur et al., 2001, 2012, 2020) makes it possible to determine the

278 age of their formation. The ratio of stable ^{88}Sr and ^{86}Sr isotopes (defined as $\delta^{88/86}\text{Sr}$ with respect
279 to NIST SRM-987 or $\delta^{88/86}\text{Sr}$) in marine carbonates generally depends on the $\delta^{88/86}\text{Sr}$ value of
280 seawater, which changes through time owing to variations in the same fluxes that control
281 seawater $^{87/86}\text{Sr}$ and the net carbonate flux from the ocean, as well as the degree of fractionation
282 between seawater and carbonate, which depends on species and temperature (Rüggeberg et al.,
283 2008; Krabbenhöft et al., 2010; Vollstaedt et al., 2014; Pearce et al., 2015; Paytan et al., 2021).
284 In the modern ocean, $\delta^{88/86}\text{Sr}$ is 0.378‰ to 0.402‰ (IAPSO standard seawater,
285 http://georem.mpch-mainz.gwdg.de/sample_query.asp). Minerals such as carbonate formed in
286 seawater are generally characterized by lower $\delta^{88/86}\text{Sr}$ than seawater because of seawater–mineral
287 fractionation. Moreover, minerals of chemogenic and biogenic origins can be distinguished by
288 the degree of their stable Sr isotope fractionation (Fietzke and Eisenhauer, 2006; Fruchter et al.,
289 2016; AlKhatib and Eisenhauer, 2017; Müller et al., 2018), which depends on temperature and
290 species. Thus, belemnites and cold-water corals do not exhibit temperature dependence of their
291 stable Sr isotope fractionation (Rüggeberg et al., 2008; Vollstaedt et al., 2014), whereas $\delta^{88/86}\text{Sr}$
292 in tropical corals increases with sea surface temperature (Fietzke and Eisenhauer, 2006;
293 Rüggeberg et al., 2008), and coccolithophores show an inverse temperature relationship
294 (Stevenson et al., 2014). In our study of Koko Guyot, warm-water corals were replaced over time
295 by deeper-water LBF and coralline algae. In our study of Koko Guyot, warm-water corals were
296 replaced over time by deeper-water LBF and coralline algae. Therefore, we expect that $\delta^{88/86}\text{Sr}$
297 will change over time in association with this species transition/replacement from warm/shallow
298 to cold/deep types. However, in the present study, it is practically impossible to predict the
299 direction of change (i.e., whether $\delta^{88/86}\text{Sr}$ will increase or decrease), due to there are many factors
300 (including sea temperature, sea salinity, and skeleton/shell growth rates) that complicate the
301 interpretation of $\delta^{88/86}\text{Sr}$ measurements.

302 Koko Guyot formed at *c.* 50 Ma (Jackson et al., 1980; Tarduno et al., 2003; Duncan and
303 Keller, 2004), and this provides a key datum for the discussion below. The mean $^{87}\text{Sr}/^{86}\text{Sr}$ ratio
304 of echinoid spines analyzed in this study is 0.70917 ± 0.00001 , which corresponds to the modern
305 isotopic water composition. Taking into account the errors associated with the LOWESS global
306 $^{87}\text{Sr}/^{86}\text{Sr}$ variation curve (McArthur et al., 2001, 2012, 2020) we infer that the age of these
307 echinoids is between 50 ka and the present (Fig. 4A). The youngest sample of unaltered
308 limestones used for isotope stratigraphy is LV86-8-4, which yielded an age of 15.30 ± 0.15 Ma
309 (Langhian, middle Miocene). Limestone sample LV86-9-1 was formed at 18.20 ± 0.15 Ma, and
310 LV86-9-4 at 19.07 ± 0.03 Ma (Burdigalian, early Miocene). Sample LV86-9-9, which is
311 composed of the remains of Merulinidae corals, formed at the Aquitanian–Burdigalian (early
312 Miocene) boundary (20.1 ± 0.3 Ma), whereas the limestone sample LV86-9-2 containing *Astrea*

313 cf. *annuligera* is Aquitanian in age (21.65 ± 0.3 Ma). The oldest studied sample, LV86-9-6, is
314 Chattian (Oligocene) in age (25.55 ± 0.45 Ma). Samples LV86-9-2, LV86-9-6, and LV86-9-9,
315 bearing *Spiroclypeus tidoenganensis* and *Heterostegina* cf. *assilinoidea*, are latest Chattian
316 (Oligocene) to Aquitanian in age. *Spiroclypeus tidoenganensis* has previously been recognized
317 from the upper Oligocene of Koko Guyot (Hottinger, 1975). Although this species has been
318 reported from coeval deposits in Saipan (Hanzawa, 1957), its Aquitanian age is firm (e.g.,
319 Hottinger, 1975; Lunt and Allan, 2007). The three limestone samples LV86-9-2, LV86-9-6, and
320 LV86-9-9 have mean ages of 21.65, 25.55, and 20.10 Ma (based on Sr isotopes), respectively,
321 consistent with the Chattian–Aquitanian age inferred from LBF species. A comparison with the
322 LOWESS 3 global $^{87}\text{Sr}/^{86}\text{Sr}$ variation curve (McArthur et al., 2001, 2012) for altered samples
323 LV86-4, LV86-8-2, and LV86-8-3 gives ages of 6.7 ± 0.3 , 26.3 ± 0.5 , and 29.2 ± 0.5 Ma,
324 respectively. The last two ages are close to the age of LV86-9-6, suggesting that samples LV86-
325 8-2 and LV86-8-3 may have approximately retained their initial compositions.

326 From 30 to 20 Ma, the $\delta^{88/86}\text{Sr}$ of seawater decreased from 0.38‰ to 0.30‰ (within
327 ± 0.02 ‰ analytical error) (Paytan et al., 2021; Fig. 4B). Five of the studied samples have ages
328 within this time interval. Two of these samples (LV86-8-2 and LV86-8-3) have probably been
329 affected by diagenetic alteration. Because diagenetic processes have been shown to alter the
330 initial $\delta^{88/86}\text{Sr}$ of carbonates (Voigt et al., 2015), we use only the three least modified samples as
331 a basis for our discussion. The $\delta^{88/86}\text{Sr}$ value of these samples varies from 0.26‰ to 0.37‰.
332 Within the margin of error (± 0.09 ‰), the results obtained intersect the line indicating the
333 isotopic composition of seawater proposed by Paytan et al. (2021). The stable Sr isotope
334 composition of younger samples from 20 to 15 Ma (LV86-8-4, LV86-9-1, and LV86-9-4)
335 comprising cold-water sea species and lacking corals is rather uniform, with the mean $\delta^{88/86}\text{Sr}$
336 varying within $0.10\text{‰} \pm 0.03\text{‰}$. These values are much lower than the isotope curve proposed
337 by Paytan et al. (2021) (Fig. 4B). The $\delta^{88/86}\text{Sr}$ values of modern echinoids are also lower than
338 (although within measurement errors of) the $\delta^{88/86}\text{Sr}$ curve.

339 It has been shown that carbonates have lower $\delta^{88/86}\text{Sr}$ Sr values than the sedimentation
340 medium, and the difference can be more than 0.1‰ (Raddatz et al., 2013, Vollstaedt et al.,
341 2014). Kisakürek et al. (2011) and Böhm et al. (2013) explained this disparity by calcification in
342 a largely open system at high precipitation rates. The shift to a benthic community that is more
343 resistant to colder water can be correlated with bottom subsidence and guyot migration to higher
344 latitudes (Wilson, 1963; Clague and Dalrymple, 1987; Tarduno et al., 2003; Clague et al., 2010).
345 The change in temperature and light regime at Koko Guyot as it subsided and migrated to higher
346 latitudes led to a change in the benthic community as reef benthic assemblages were replaced by
347 those dominated by LBF (and coralline algae). The change in temperature and light regime at

348 Koko Guyot as it subsided and migrated to higher latitudes led to a change in the benthic
349 community as reef assemblages were replaced by those dominated by LBF and coralline
350 algae. We presume that this change in benthic community is recorded as a sharp decrease in
351 $\delta^{88/86}\text{Sr}$ values in our samples compared to sea water (Fig. 4B) without major changes in
352 seawater $\delta^{88/86}\text{Sr}$ values. It is probable that Sr isotope fractionation between cold-water species
353 and ambient seawater is much stronger than that between warm-water species and ambient
354 seawater. However, we cannot take into account temperature and depth changes in this paper.

355

356 4.2. Rate of subsidence of Koko Guyot and its variation over time

357

358 Grigg (1988) identified corals *Favites* sp., *Platygyra* sp., *Psammocora* (*Stephanaria*) sp.,
359 and *Seriatopora* sp. from Koko Seamount, the ages of which ranged from 30.5 to 24.7 Ma, as
360 determined using Sr isotope stratigraphy. Clague et al. (2010) obtained ages for corals ranging
361 from 50 to 27 Ma, compared with 16 Ma for LBF, on the basis of which those authors calculated
362 the subsidence rate of the volcano as 0.012 ± 0.003 mm/yr. Davies et al. (1972) used water
363 depth, guyot structure, and the age and species composition of corals to estimate the subsidence
364 rate of Koko Guyot as 0.042 mm/yr throughout the existence of the guyot.

365 Our method of estimation of subsidence rates for Koko Guyot incorporated the following
366 assumptions: (1) reef formation slowed and then stopped owing to submersion below the
367 euphotic zone, which is the lower depth limit of coral and algal growth; (2) the identified fossil
368 benthic assemblage from the guyot plateau lived in optimal depth (i.e., 0–30 m) and temperature
369 (average winter water temperature >18 °C) conditions for reef growth (Veron, 1995); and (3)
370 later benthic communities, devoid of reef corals, lived at greater water depths >30 m. Warm-
371 water corals grow at a certain depth, no more than 30 m (Veron, 1995). As the seafloor subsides
372 and relative sea-level rise resultantly occurs, the reef builds up vertically to retain a zone of
373 maximum favorability for coral existence. We took the maximum water depth of this zone for
374 corals in this study as 30 m. We also assumed that the formation of the carbonate skeleton
375 occurred under normal conditions. With gradual subsidence of the seafloor, we assumed that the
376 reef of Koko Guyot was able to keep up with sea-level rise so long as the seafloor was within the
377 euphotic zone. As the rate of sinking increased, new colonies would have formed more quickly
378 to grow to a favorable depth (maximum 30 m). With a high subsidence rate, the coral growth
379 rate will also be faster. The «new» corals will record the «new» isotopic composition of water.
380 Thus, samples with a small difference in age will occur more often. Thus, we have described our
381 «model object» and proceed to the calculations.

382 We took all age estimates (Grigg, 1988; Clague et al., 2010; this work), ranked them from
383 youngest to oldest, and calculated the difference between each successive age (which ranged
384 from 0 to 2 Myr), thus obtaining 26 datapoints (Table 5 and Fig. 5). Figure 5 shows that the age
385 difference between the samples during the early stage of guyot evolution is small and that this
386 difference increases with Koko Guyot age. The pattern of data in Fig. 5 suggests that the rate of
387 reef growth (or of the guyot's subsidence) varied over time. The age difference for the period
388 30–25 Ma is smaller than that for 25–15 Ma, suggesting that the reef grew more quickly during
389 the older period. The age of the youngest identified coral specimen is 20.1 ± 0.3 Ma (LV86-9-9).
390 This sample may therefore mark the final episode of active reef growth, after which the platform
391 deepened to a position below the euphotic zone (Wilson, 1963; Clague and Dalrymple, 1987;
392 Tarduno et al., 2003; Clague et al., 2010). We also sampled a coralline algal crust dated at 15 Ma
393 (LV86-8-4). The sample was collected from a depth of 1458 m, where it was located in a soft
394 (unconsolidated) substrate. This sample most likely slid down the slope from the nearest plateau,
395 whose current top height is at 350 m water depth. Assuming a maximum water depth of 120 m
396 for the living coralline algae and 30 m for the living youngest zooxanthellate corals sampled
397 (Clague et al., 2010), we calculated the following: (1) From 15 Ma to the present, Koko Guyot
398 subsided at a rate of $(350 - 120)/15.3 = 15.0$ m/Myr, that is, 0.015 ± 0.002 mm/yr; and (2) during
399 the period from 20 to 15 Ma, the mean subsidence rate was $(120 - 30)/(20.1 - 15.3) = 18.8$
400 m/Myr, that is, 0.019 ± 0.003 mm/yr. A previous study has suggested that the initial shallow-
401 water sediments formed during the period from 49.7 to 43.5 Ma, as identified in the ODP Site
402 1206 (Fig. 1) core recovered at 1500 m water depth (Shipboard Scientific Party, 2002). The
403 bottom of this layer was 57 m from the top of the column (Shipboard Scientific Party, 2002;
404 Tarduno et al., 2003). Thus, applying our calculation method, the subsidence rate during the first
405 tens of million years (from 49.7 to 43.5 Ma) is estimated as 0.046 ± 0.005 mm/yr [using $(1500 +$
406 $57 - 350)/(46.6 - 20.1) = 46.2$ m/Myr or 0.046 ± 0.005 mm/yr, where 46.6 Ma is the mean of
407 49.7 and 43.5 Ma] (Fig. 6), which is close to the rate reported by Davies et al. (1972). Our
408 calculated average subsidence rate is higher than that estimated by Clague et al. (2010) of 0.008–
409 0.012 mm/yr since 23 Ma. However, our results are consistent with the observation that the
410 subsidence rate of the ocean floor decreases as the age of the ocean crust increases (e.g., Sclater
411 et al., 1980; Marty and Cazenave, 1989; Stein and Stein, 1992). This process represents seafloor
412 flattening, meaning that old seafloor is shallower than that predicted by the “root-t” model (i.e., a
413 linear increase in ocean depth with increasing crustal age; Parsons and Sclater, 1977; Hillier,
414 2010).
415
416

417 **5. Conclusions**

418

419 We investigated the Sr isotope compositions of Oligocene–Miocene coral reef limestone
420 from Koko Guyot in the southern Emperor Seamount Chain to assess the dynamics of the
421 subsidence of this guyot. Our study of Sr isotope compositions ($^{87}\text{Sr}/^{86}\text{Sr}$) showed that the least
422 altered limestones containing fragments of reef corals were formed during the early Miocene. No
423 coral fragments were found in older samples (late Oligocene). Analysis of the distribution of
424 stable Sr isotopes ($\delta^{88/86}\text{Sr}$) in warm-water sediments showed a low degree of fractionation
425 compared with seawater. The $\delta^{88/86}\text{Sr}$ values of cold-water species, which replaced warm-water
426 species at around 20 Ma, differ significantly from the seawater $\delta^{88/86}\text{Sr}$ variation curve estimated
427 by Paytan et al. (2021).

428 Using several independent methods, we confirmed a change in environmental parameters
429 at around 20 Ma. This timing also corresponds to a change in the rate of subsidence. From 49–44
430 to 20 Ma, the subsidence rate of Koko Guyot was 0.046 ± 0.005 mm/yr. The $\delta^{88/86}\text{Sr}$ values of
431 coral samples that formed from 25 to 20 Ma vary from 0.26‰ to 0.37‰ (± 0.09 ‰) and are
432 consistent with the variation curve proposed by Paytan et al. (2021). At the ending of this period,
433 the benthic community changed because of cooling ambient waters. Warm-water corals
434 disappeared and were replaced by LBF and coralline algae. From 20 to 15 Ma, the subsidence
435 rate was much lower at 0.019 ± 0.003 mm/yr. The $\delta^{88/86}\text{Sr}$ values for samples that formed during
436 this period are ~ 0.10 ‰. Since 15 Ma, the volcanic structure has subsided at a rate of $0.015 \pm$
437 0.002 mm/yr. The data obtained in this study refine existing models of the crustal subsidence of
438 the floor of the Pacific Ocean, which suggest a constant rate of seafloor subsidence.
439 Understanding the changing rate of subsidence is important because it is related to the process of
440 ocean-floor cooling after the Pacific Plate passed over the mantle Hawaiian hotspot.

441

442 **Declaration of competing interests**

443

444 The authors declare that they have no known competing financial interests or personal
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446

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467

468 **Data availability**

469 All data are provided in attached files and at <https://doi.org/10.5281/zenodo.6330970>.

470

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667
668

669 **Figure and table captions**

670

671 Fig. 1. (A) Geographic map of the Hawaiian–Emperor bend. (B) Bathymetric map of Koko
672 Guyot. Points represent sampling sites for dives 4, 8, 9, and 16. Deep Sea Drilling Project sites
673 308 and 309 and Ocean Drilling Program Site 1206 are shown by value. The source of the
674 bathymetric map is <http://earthref.org>.

675

676 Fig. 2. Photographs of sampling conducted by a Comanche remotely operated underwater
677 vehicle. (A) Rock sampling from the plateau of the guyot using a manipulator (dive 9; sample
678 Lv86-9-2); (B) Sampling using a scoop net mounted on the manipulator (dive 9; sample Lv86-9
679 echinoid).

680

681 Fig. 3. (A) Modern octocoral of the Isididae family (sample Coral). (B) Echinoderm spines
682 (Cidaroida; sample LV86-9, echinoid). (C–D) Larger-foraminiferal packstone with *Spiroclypeus*
683 *tidoenganensis* (*St*) and *Heterostegina* cf. *assilinoidea* (*Ha*) (samples Lv86-9-2 and Lv86-9-6).
684 (E) Reef coral *Astrea* cf. *annuligera* (sample Lv86-9-2; i, thickened costo-septum; ii, paliform
685 lobe). (F–G) Bioclastic packstone showing (F) the encrusting coralline *Lithoporella* sp. with two
686 uniporate conceptacles (arrows; sample LV86-8-3; conc., conceptacle) and (G) bryozoans (bry)
687 and coralline fragments (cor; sample LV86-9-4).

688

689 Fig. 4. Comparison of the Sr isotopic composition of the studied samples with (A) the radiogenic
690 Sr isotope record (LOWESS 3; McArthur et al., 2001) and (B) a model of the stable Sr isotope

691 record with $\pm 0.02\%$ analytical uncertainty (gray area; Paytan et al., 2021) in the ocean. Crossed-
692 out circles represent data from diagenetically altered samples. Error bars are $\pm 0.09\%$.

693

694 Fig. 5. Relationship between age and age difference between two consecutive ages for carbonate
695 samples. The difference between the ages of consecutive older samples is less than that of the
696 younger samples. This suggests that the rate of subsidence of the reef superstructure was initially
697 high and subsequently decreased (i.e., the subsidence rate was higher when the coral reef and the
698 guyot were younger). Data from this work (circles), Grigg (1988, diamonds), and Clague et al.
699 (2010, squares) are plotted in the figure.

700

701 Fig. 6. Schematic model for the vertical motion of Koko Guyot. The bold line in the graph shows
702 the changing position of the summit of the volcano, which formed at 49–48 Ma (Jackson et al.,
703 1980; Tarduno et al., 2003; Duncan and Keller, 2004). The rates given in the figure indicate the
704 subsidence rate, calculated using the method presented in Section 4.2.

705

706 Table 1. Coordinates and depth of samples analysed in this study, and seawater temperature and
707 salinity at the sampling sites.

708 T, water temperature; S, salinity; Coral, sample of modern isididae coral; echinoid, sample of
709 echinoid spines

710

711 Table 2. Lithology and biotic components from the studied Koko Guyot carbonate samples.

712

713 Table 3. Trace-element contents and calculated Fe/Sr and Mn/Sr ratios of the studied carbonates.
714 Analyses were performed using ICP–AES. Contents are given in ppm.

715

716 Table 4. Strontium isotope compositions and ages according to LOWESS 3 (McArthur et al.,
717 2001, 2012).

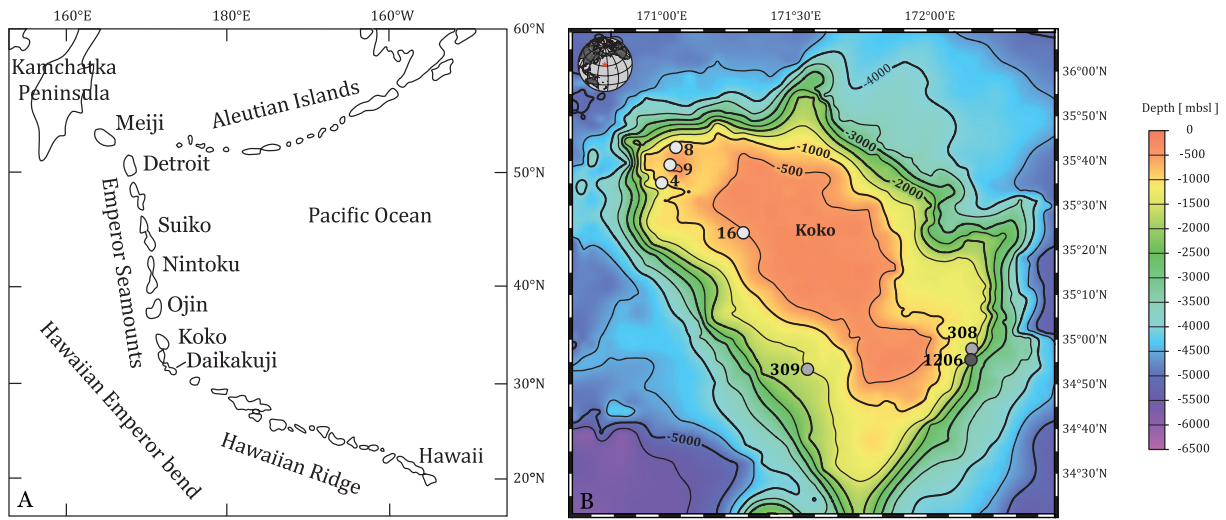
718

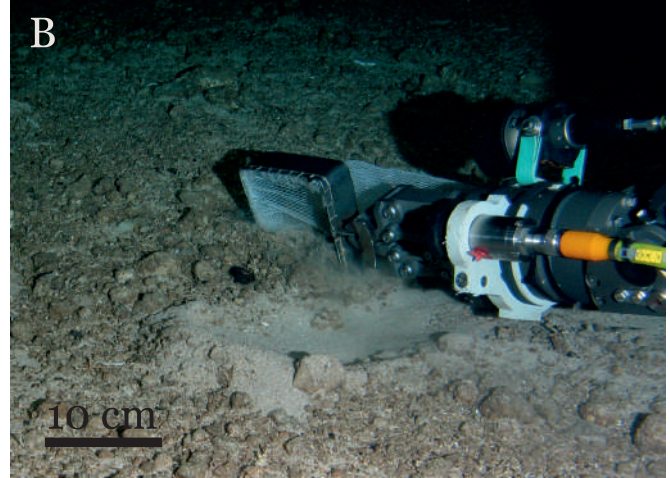
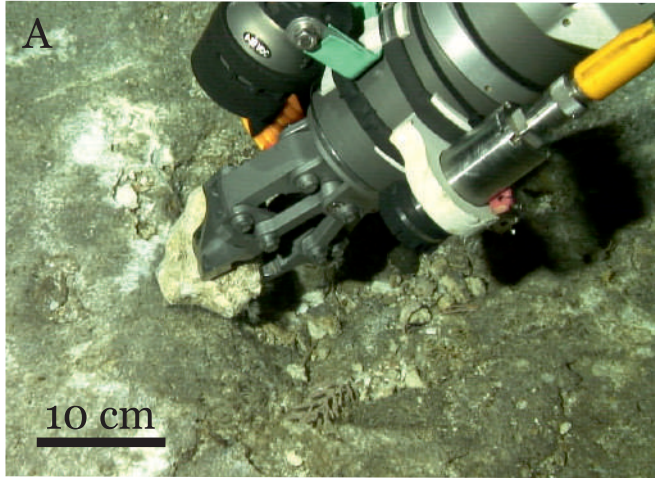
719 Table 5. Strontium isotope ages of samples from the present study and previous studies (blue,
720 Grigg, 1988; yellow, Tarduno et al., 2003; green, Clague et al., 2010; white, this study) used to
721 calculate age differences between consecutive samples.

722

Figure 1

[Click here to access/download;Figure;Fig 1 Map 22-07-17.eps](#)





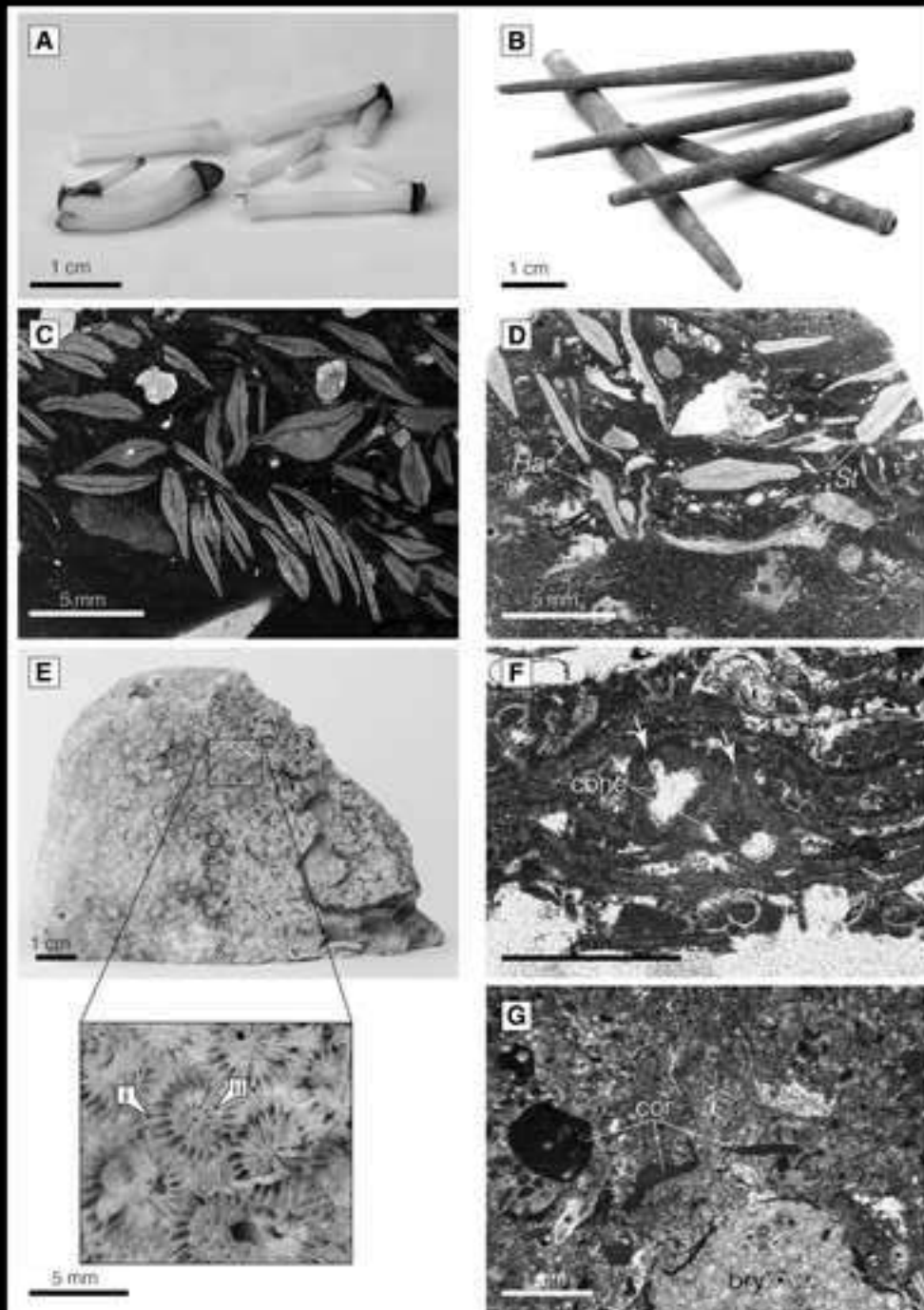
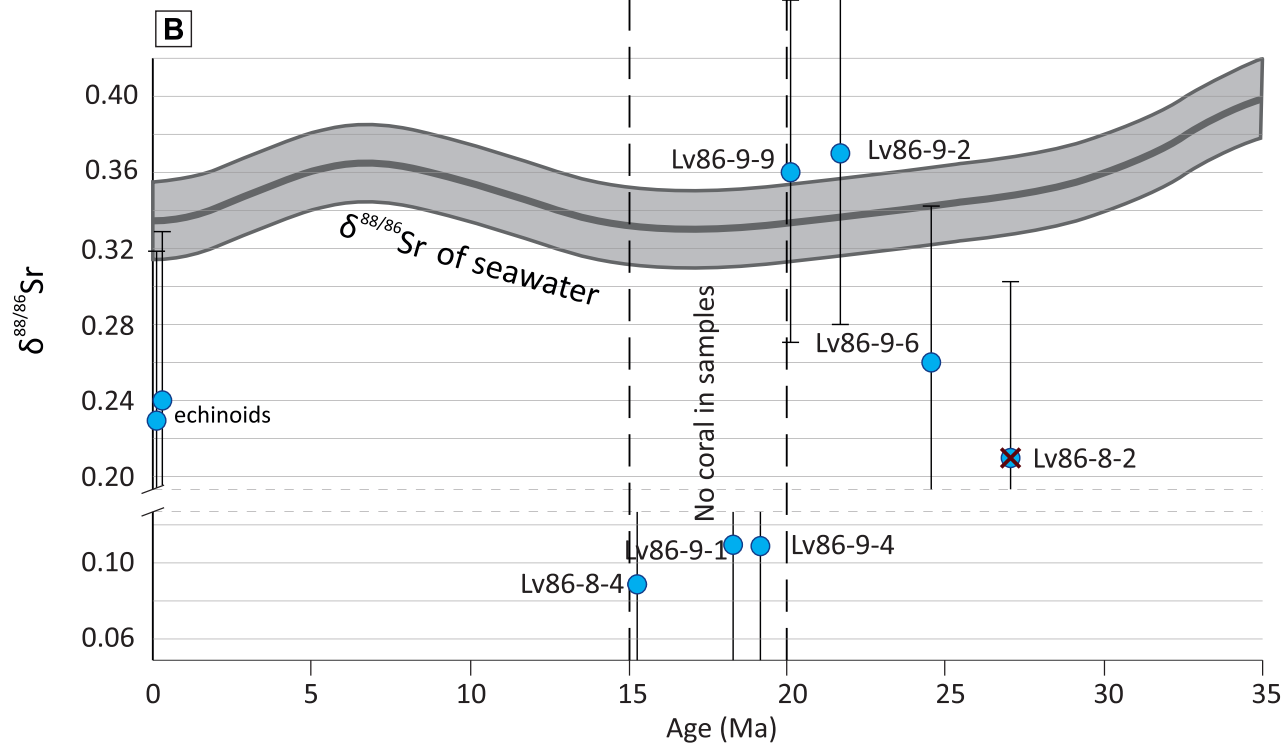
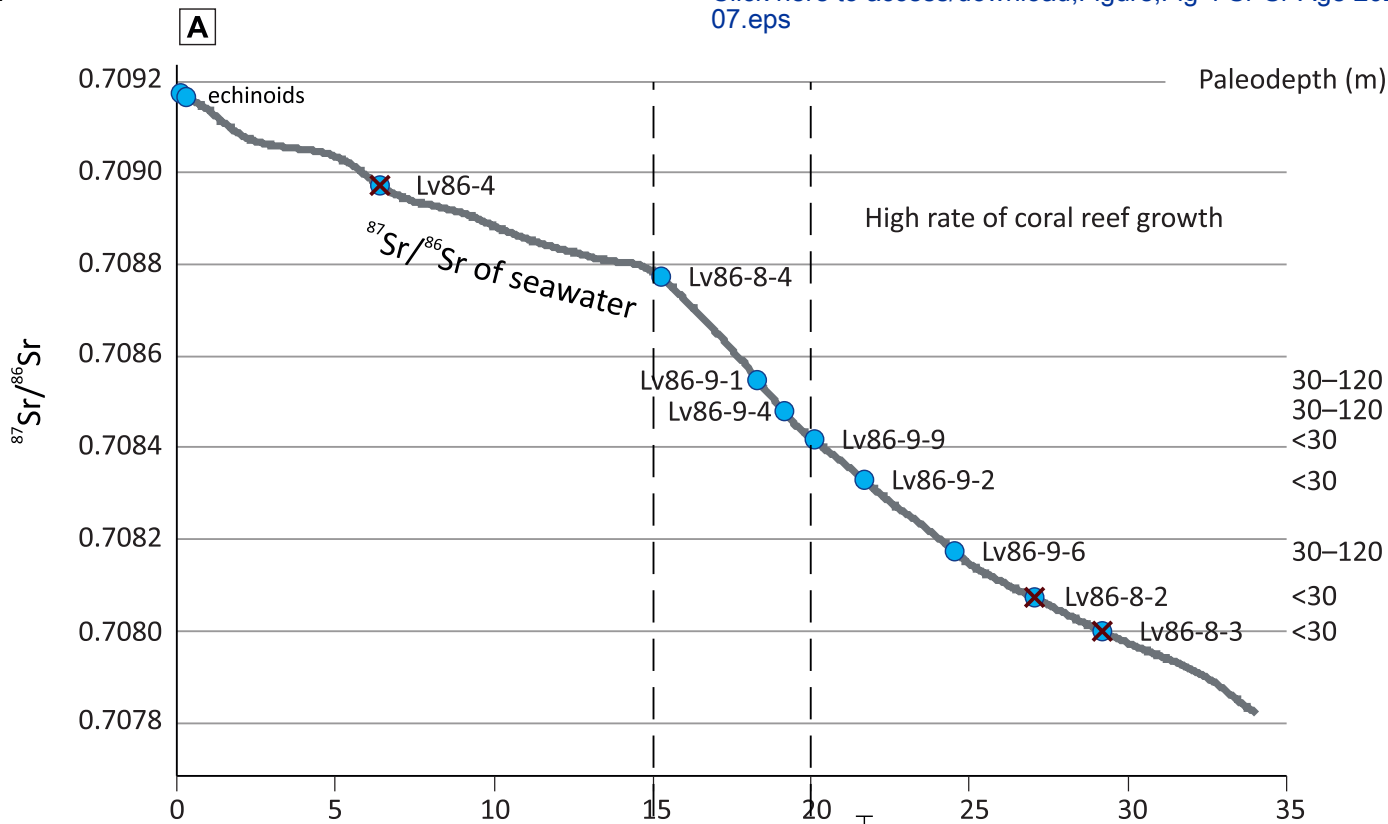
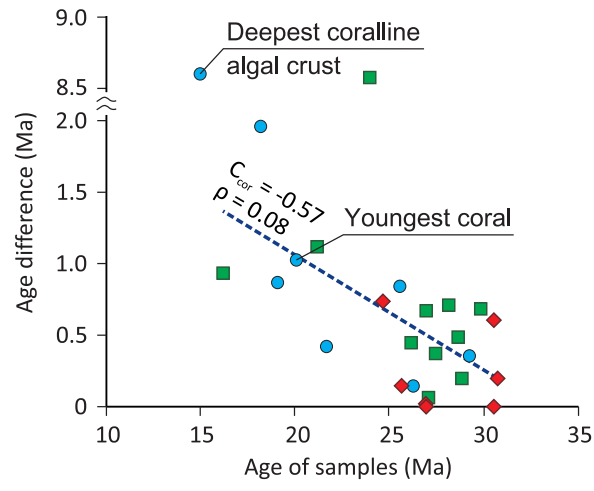
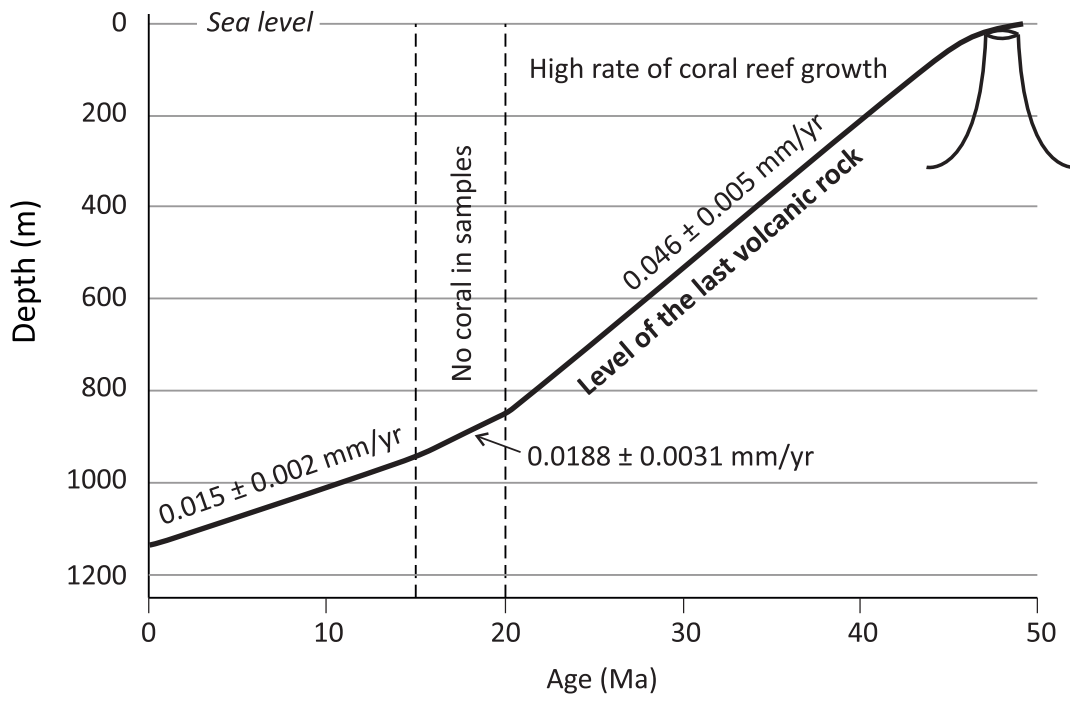


Figure 4







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Table 1. Coordinates and depth of samples analysed in this study, and seawater temperature and salinity at the sampling sites.

Dive	Sample	Coordinate	Depth (m)	T (°C)	S
4	LV86-4	35.58365°N; 171.24615°E	487	10.3	34.18
4	Coral	35.71235°N; 171.07082°E	578		
8	LV86-8-2	35.71235°N; 171.07082°E	578		
8	LV86-8-3	35.71235°N; 171.07082°E	578	6.49	34
8	LV86-8-4	35.76769°N; 171.06696°E	1458	3.03	34.39
9	LV86-9 echinoid	35.65593°N; 171.05479°E	357		
9	LV86-9-1	35.65593°N; 171.05479°E	357		
9	LV86-9-2	35.65593°N; 171.05479°E	357	13.66	34.49
9	LV86-9-4	35.65625°N; 171.05437°E	374		
9	LV86-9-6	35.65699°N; 171.05472°E	360		
9	LV86-9-9	35.67756°N; 171.05456°E	357		
16	LV86-16 echinoid	35.40487°N; 171.32104°E	387	12.97	34.41

T, water temperature; S, salinity; Coral, sample of modern Isididae coral; echinoid, sample of echinoid spines

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Table 2. Lithology and biotic components from the studied Koko Guyot carbonate samples.

Dive	Sample	Description
8	LV86-8-2	Piece of coral Merulinidae? species
8	LV86-8-3	Rhodolith composed of encrusting coralline algae (e.g., <i>Lithoporella</i> sp.) with nuclei consisting of molluscan shells
8	LV86-8-4	Bioclastic packstone with very fine to fine sand-sized bioclasts (dominated by ostracods). Bivalves and bryozoans are subordinate
9	LV86-9-1	Larger benthic foraminifera (LBF) floatstone with coralline algal crusts (melobesioids)
9	LV86-9-2	Larger foraminiferal packstone with subordinate bryozoans, coralline algae, and bivalves. <i>Astrea</i> cf. <i>annuligera</i> are present. The matrix is composed of very fine to fine sand-sized bioclasts (rich in ostracods) with a matrix of clotted micrite
9	LV86-9-4	Fine bioclastic packstone with LBFs, coralline algal (melobesioids) fragments, and bryozoans
9	LV86-9-6	Bioclastic floatstone with gravel-sized bioclasts of LBFs (<i>Spiroclypeus tidoenganensis</i> and <i>Heterostegina assilinoidea</i>), bivalves, coralline algae, and bryozoans
9	LV86-9-9	Bioclastic LBF floatstone (<i>Spiroclypeus tidoenganensis</i> and <i>Heterostegina</i> cf. <i>assilinoidea</i>) and bivalves (mostly oyster), undetermined merulinid corals, and <i>Porites</i> sp.

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Table 3. Trace-element contents and calculated Fe/Sr and Mn/Sr ratios of the studied carbonates. Analyses were performed using ICP–AES. Contents are given in ppm.

Sample	Fe	Al	Mn	Mg	Sr	Fe/Sr	Mn/Sr
Coral	60	40	20	14330	2300	0.026	0.009
LV86-9 echinoid	40	110	10	4500	1300	0.031	0.008
LV86-16 echinoid	180	300	40	5470	1200	0.150	0.033
LV86-4	740	150	130	4850	1000	0.740	0.130
LV86-8-2	230	210	110	3940	300	0.767	0.367
LV86-8-3	30	80	180	3790	300	0.100	0.600
LV86-8-4	20	70	30	4230	500	0.040	0.060
LV86-9-1	10	50	10	7090	400	0.025	0.025
LV86-9-2	20	40	20	3880	230	0.087	0.087
LV86-9-4	20	60	20	4660	280	0.071	0.071
LV86-9-6	10	60	30	3410	300	0.033	0.100
LV86-9-9	10	50	30	3860	300	0.033	0.100

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Table 4. Strontium isotope compositions and ages according to LOWESS 3 (McArthur et al., 2001, 2012).

Sample	$\delta^{88/86}\text{Sr}$ (‰)	SE, abs	$^{87}\text{Sr}/^{86}\text{Sr}$	SE, abs	Minimum age (Ma)	Maximum age (Ma)	Median age (Ma)
Coral	-0.06	0.01	0.709108	0.000008			
LV86-9 echinoid	0.24	0.01	0.709174	0.000007			
LV86-16 echinoid	0.23	0.01	0.709173	0.000008			
LV86-4	-0.05	0.01	0.708961	0.000006	6.40	7	6.70
LV86-8-2	0.21	0.01	0.708064	0.000007	26.85	27.75	26.30
LV86-8-3	-0.03	0.01	0.708000	0.000006	28.75	29.65	29.20
LV86-8-4	0.09	0.01	0.708771	0.000006	15.10	15.45	15.30
LV86-9-1	0.11	0.01	0.708557	0.000006	18.05	18.35	18.20
LV86-9-2	0.37	0.01	0.708330	0.000010	21.35	21.95	21.65
LV86-9-4	0.11	0.01	0.708482	0.000006	19.05	19.10	19.07
LV86-9-6	0.26	0.04	0.708173	0.000020	24.05	25.10	25.55
LV86-9-9	0.36	0.01	0.708415	0.000006	19.85	20.40	20.10

SE, standard error in absolute value

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Table 5. Strontium isotope ages of samples from the present study and previous studies (blue, Grigg, 1988; yellow, Tarduno et al., 2003; green, Clague et al., 2010; white, this study) used to calculate age differences between consecutive samples.

Sample	Age (Ma)	error	Paleodepth (m)	Modern depth (m)	Ranked data			
					Sample	Age (Ma)	error	Age difference (Ma)
this work					LV86-4	6.7	0.30	
LV86-4	6.7	0.3	>120	487	LV86-8-4	15.30	0.15	8.60
LV86-8-4	15.30	0.15	30–120	1458	A8	16.24	0.15	0.94
LV86-9-1	18.20	0.15	30–120	357	LV86-9-1	18.20	0.21	1.96
LV86-9-4	19.07	0.03	30–120	374	LV86-9-4	19.07	0.03	0.87
LV86-9-9	20.1	0.30	30	357	LV86-9-9	20.1	0.30	1.03
LV86-9-2	21.65	0.30	30–120	357	A23	21.22	0.22	1.12
LV86-9-6	25.55	0.45	30–120	360	LV86-9-2	21.65	0.30	0.43
LV86-8-3	29.2	0.50	30–120	578	A26	23.96	0.28	2.31
LV86-8-2	26.3	0.50	30	578	Favia sp. 1	24.7		0.74
Grigg, 1988					LV86-9-6	25.55	0.45	0.85
Favia sp. 1	24.7		20	624–823	Favia sp. 2	25.7		0.15
Favia sp. 2	25.7		20	624–823	A32	26.15	0.50	0.45
	30.7		20	624–823	LV86-8-2	26.3	0.50	0.15
Favites sp. 1	27		20	624–823	A22	26.97	0.43	0.67
Favites sp. 2	30.5		20	624–823	Favites sp. 1	27		0.03
Platygyra sp.	30.5		20	624–823	Seriatopora sp.	27		0.00
Seriatopora sp.	27		20	624–823	A12	27.07	0.47	0.07
Clague et al., 2010					A18	27.44	0.44	0.37
A5	28.64		20	624–823	A19	28.15	0.33	0.71
A6	29.89	0.43	20	624–823	A5	28.64		0.49
A8	16.24	0.21	120	624–823	A20	28.84	0.36	0.20
A12	27.07	0.47	20	624–823	LV86-8-3	29.2	0.50	0.36
A18	27.44	0.44	20	624–823	A6	29.89	0.43	0.69
A19	28.15	0.33	20	624–823	Favites sp. 2	30.5		0.61
A20	28.84	0.36	20	624–823	Platygyra sp.	30.5		0.00
A22	26.97	0.43	20	624–823		30.7		0.20
A23	21.22	0.22	20	624–823	Oldest sediment	43.5		12.80
A26	23.96	0.28	20	624–823				
A32	26.15	0.50	20	624–823				
Tarduno et al., 2003								
Oldest sediment	43.5							

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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1 Sr isotope variations in Oligocene–Miocene and modern biogenic carbonate
2 formations of Koko Guyot (Emperor Seamount Chain, Pacific Ocean)

3

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26

27 ABSTRACT

28

29 The Hawaiian–Emperor Seamount Chain, a major topographic feature of the Pacific Ocean
30 floor, is composed of seamounts capped with fossil coral reef deposits ~~that formed~~ originally
31 ~~formed~~ close to sea level but ~~are now lying today covered by~~ hundreds of meters ~~in of~~ water
32 ~~depth due owing~~ to prolonged subsidence. These fossil reef deposits are important archives of
33 paleoenvironmental change^s and yield information on the subsidence history of the seamounts.
34 We studied ~~the~~ Sr isotope compositions of Oligocene–Miocene coral reef limestone from Koko

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35 Guyot in the southern ~~part of the~~ Emperor Seamount Chain ~~in order~~ to assess the dynamics of the
 36 subsidence ~~dynamics~~. ~~The age~~ The ages of the studied samples with containing coral fragments
 37 established by Sr isotope stratigraphy varies from 26.3 to 20.1 Ma. ~~In contrast,~~ ~~while~~ the
 38 youngest samples (15.3 Ma), which were deposited at in water depths of water depth of >120 m,
 39 are barren ~~in of~~ corals and are composed exclusively of bryozoans and coralline algae, are 15.3
 40 Ma in age. The subsidence rate of the Koko Guyot volcanic structure was not ~~uniform constant~~
 41 over time. ~~Combining data of previous studies and those obtained in this study~~. Integration of our
 42 new data with the results of previous studies reveals that the ~~assessed~~ subsidence rate was
 43 0.046 ± 0.005 mm/yr during the first 25–30 Myr (from 49–44 to 20 Ma ~~from 49–44 Ma)~~,
 44 During this period ~~of time~~, Koko Guyot was in a bathymetric interval favourable for coral reef
 45 development, ~~and~~ its subsidence was compensated by rapid vertical growth of the reef ~~growth~~.
 46 Successively Subsequently, the subsidence rate decreased to an average value of 0.019 ± 0.003
 47 mm/yr from 20 to 15 Ma. The decrease in the rate of bottom subsidence coincided with
 48 unfavourable environmental conditions for coral reef development, leading to the disappearance
 49 of corals. The average subsidence rate reached a value of has been 0.015 ± 0.002 mm/yr in the
 50 last since 15 Ma, comparable ~~to to~~ the present-day subsidence rate. ~~The $\delta^{88/86}\text{Sr}$ value of the~~
 51 studied samples, which are represented by fragments of warm-water corals and formed 25–20
 52 Ma ago, corresponds to that in the generalized $\delta^{88/86}\text{Sr}$ variation curve in the World Ocean
 53 (0.32 ± 0.1‰ vs. 0.34 ± 0.03‰). More recent carbonates, which are formed by Larger benthic
 54 foraminifera, and coralline algal, and other non-coral species, have $\delta^{88/86}\text{Sr}$ well below this curve
 55 (about 0.10 ± 0.09‰ vs. 0.33 ± 0.02‰), which we attribute this fractionation to change in
 56 environmental and in biocommunity. We also analyzed the stable Sr isotope ratios ($\delta^{88/86}\text{Sr}$) of
 57 warm-water coral samples formed at 25–20 Ma (0.32‰ ± 0.1‰), as well as carbonate of large
 58 benthic foraminifera, coralline algae, and other non-coral species for the period 20–15 Ma
 59 (0.10‰ ± 0.09‰). We suggest that the large difference in carbonate $\delta^{88/86}\text{Sr}$ between 25–20 and
 60 20–15 Ma corresponds to a difference in the fractionation factor caused by environmental and
 61 benthic community change.

62
 63 *Key words:*

64 $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, $\delta^{88/86}\text{Sr}$, Corals, Bryozoans, Larger foraminifera, Subsidence, Hawaiian–Emperor
 65 Seamount Chain, Hawaiian hotspot

66
 67 **1. Introduction**
 68

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69 The Emperor Seamount Chain (Pacific Ocean) includes more than a dozen seamounts
70 (i.e., extinct volcanoes). The northernmost ~~seamount of~~ Meiji ~~Seamount~~ is considered the
71 oldest, with an age estimated at 85 Ma (Keller et al., 2000). The youngest ~~seamount of~~
72 Daikakuji ~~Seamount~~ (42 Ma; Dalrymple and Clague, 1976) is located at the junction ~~of the~~
73 ~~Emperor Seamount Chain~~ with the Hawaiian Seamount Chain (Fig. 1). ~~Koko Guyot is the~~
74 ~~southernmost seamount and one of the largest in the Emperor Seamount Chain with a surface~~
75 ~~area of 5.800 km² (Greene et al., 1980). It is located from 34° to 36.5° N and from 170.8° to~~
76 ~~171.5° E. The top of the guyot, located at a depth of 270 m from the sea level (Matter, Gardner,~~
77 ~~1975), is characterize by a predominantly flat upper part at 300–400 m water depth.~~

78 The Emperor–Hawaiian Seamount Chain formed as a result of the prolonged activity of
79 the so-called Hawaiian ~~Hot Spot~~ ~~hotspot~~, a long-lived mantle plume beneath the Pacific Plate
80 (Jackson et al., 1980; Clague and Dalrymple, 1987; Tarduno et al., 2003; and references therein).
81 Plate movement relative to conventionally stationary mantle structure led to the formation of a
82 linear chain of volcanic islands and seamounts with ages increasing from south to north. The
83 seamounts situated in ~~the south of the~~ ~~the southern~~ Emperor Seamount Chain are topped with a
84 sediment cover containing carbonate rocks (Shipboard Scientific Party, 1975a, 1975b, 2002),
85 which represent an excellent geochemical, paleontological, and paleogeographic ~~settings~~.

86 ~~The following development sequence for seamounts has been established (Wheeler and~~
87 ~~Aharon, 1991). After the cessation of volcanic activity, a coral reef began to develop on the~~
88 ~~volcanic island (Wheeler and Aharon, 1991). Over time, the volcano subsided, and the coral reef~~
89 ~~at first kept pace with relative sea-level rise by enlarging upward. As the oceanic crust moved~~
90 ~~away from the area of plume activity and cooled, the volcano subsided further, and the coral reef~~
91 ~~(which was unable to keep up with sea-level rise) drowned. The~~ ~~Although the main~~ cause of
92 ~~drowning the demise of the coral could be was the rapid~~ a relative sea-level rise ~~to, o~~ fast for the
93 ~~coral reef to keep up, but it could also be related to the other factors such as a decrease in sea~~
94 ~~surface temperature as the volcanic island migrated to higher latitudes by plate motion may also~~
95 ~~have been influential (e.g., Clague et al., 2010). decrease in sea surface temperature (SST) as the~~
96 ~~volcanic island migrated to higher latitudes or combination of several factors (e.g., Clague et al.~~
97 ~~(2010)); migration in cooler waters, global cooling trend, combined with slow subsidence.~~

98 ~~Based on all available information, the speed and direction of movement of the hotspot~~
99 ~~and the Pacific plate have been established. Koko Guyot and the hotspot diverged in different~~
100 ~~directions: the seamount to the north, the hotspot to the south (Wilson, 1963; Clague and~~
101 ~~Dalrymple, 1987; Tarduno et al., 2003). Clague et al. (2010) studied corals in southern Koko~~
102 ~~Guyot, and used Sr isotope stratigraphy to date the carbonates. According to their calculation, in~~
103 ~~the first 5 Ma of its existence, Koko Guyot was migrating at a rate of 69 km Myr⁻¹ and the guyot~~

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104 moved from 21.5°N to 23°N. In addition, the authors also show that the rate at which Koko
105 Guyot migrated decreased to 31 km Myr⁻¹ between 45 Ma and the present, and that the direction
106 of movement changed to the north-west before reaching its present position at latitude 35°N.
107 Clague et al. (2010) propose a two-phase subsidence history: (1) ~0.009 mm yr⁻¹ from 27.1 to
108 16.2 Ma, and (2) ~0.014 mm yr⁻¹ from 16.2 Ma to the present. They also suggest that the timing
109 of reef growth cessation at Koko Guyot occurred around 29 Ma, based on the youngest age of
110 corals they sampled (i.e., 27 Ma), and the average subsidence rate they calculated (i.e., 0.012 mm
111 yr⁻¹). Data regarding the speed and direction of movement of the Hawaiian hotspot and the
112 Pacific Plate show that the paths of Koko Guyot and the hotspot diverged (c. 45 Ma), whereby
113 the seamount moved to the north and the hotspot moved to the south (Wilson, 1963; Clague and
114 Dalrymple, 1987; Tarduno et al., 2003). Clague et al. (2010) studied corals in southern Koko
115 Guyot and used Sr isotope stratigraphy to date the carbonates. According to those authors'
116 calculations, Koko Guyot migrated northward at a rate of 69 km/Myr during the first 5 Myr (c.
117 50–45 Ma) of its existence, moving from 21.5° to 23°N. In addition, the rate at which the guyot
118 migrated decreased to 31 km/Myr between 45 Ma and the present, and the direction of
119 movement changed to the northwest before reaching its present position at 35°N. Clague et al.
120 (2010) proposed a two-phase subsidence history for Koko Guyot: (1) ~0.009 mm/yr from 27.1 to
121 16.2 Ma; and (2) ~0.014 mm/yr from 16.2 Ma to the present. Those authors also suggested that
122 the timing of reef growth cessation at Koko Guyot occurred at c. 29 Ma, on the basis of the
123 youngest age of sampled corals (27 Ma) and the calculated average subsidence rate (0.012
124 mm/yr).

125 We studied samples from the northwestern part of the Koko Guyot, where sampling had
126 not been carried out so far. We used a new sampling method for this region—a remotely
127 controlled underwater vehicle (see Methods), so our samples are geographically and
128 bathymetrically referenced. As part of our study, we did not want to refute previous studies, we
129 wanted to check them and, if possible, improve them, which is why the samples were taken from
130 a place remote (but not very much) from the area of previous works. The aim of this study is to
131 establish the youngest age limit of coral reefs on Koko Guyot, and to perform further constrains
132 of the timing of coral reef drowning as Koko Guyot was submerged. Moreover, in order to
133 improve the understanding of the subsidence history of Koko Guyot, we use the difference in the
134 age of sampled corals and their bathymetry to calculate the average subsidence rate of this
135 volcanic structure. To achieve these goals, we performed a paleontological analysis and a study
136 of the Sr isotope composition of samples collected from the Koko Guyot. We compared the
137 obtained ⁸⁷Sr/⁸⁶Sr ratios with the curve of variation of this value in the Cenozoic (McArthur et
138 al., 2001, 2020). In addition, we use the $\delta^{88/86}\text{Sr}$ record measured in carbonates as a proxy for an

139 ~~environmental change on the flooded reef platform.~~ We studied samples obtained from the
140 ~~northwestern part of Koko Guyot, where sampling has hitherto not been conducted. We used a~~
141 ~~new sampling method for this region, namely, a remotely controlled underwater vehicle (see~~
142 ~~“Material and Methods”), so our samples could be geographically and bathymetrically~~
143 ~~referenced. Our purpose was to confirm the previous estimates of coral age and subsidence rate~~
144 ~~made by Clague et al. (2010) with samples taken from a site distant from the area of previous~~
145 ~~work and, if possible, improve the estimates by measuring isotope ratios using a different type of~~
146 ~~equipment (a Neptune Plus multicollector inductively coupled plasma mass spectrometry (ICP–~~
147 ~~MS) instrument versus a VG Sector 54 Thermal ionization mass spectrometer (TIMS) in Clague~~
148 ~~et al. (2010)) and reducing uncertainties in age estimates. The aim of the study was to establish~~
149 ~~the youngest age limit of coral reefs on Koko Guyot and further constrain the timing of coral reef~~
150 ~~drowning as Koko Guyot became submerged. In addition, to improve the understanding of the~~
151 ~~subsidence history of Koko Guyot, we used differences in the ages of sampled corals and their~~
152 ~~depths to calculate the average subsidence rate of this volcanic structure for different periods. To~~
153 ~~achieve these aims, we performed paleontological analysis and measured the Sr isotope~~
154 ~~compositions of samples collected from the Koko Guyot. We compared the obtained $^{87}\text{Sr}/^{86}\text{Sr}$~~
155 ~~ratios with the variation curve of this ratio for the Cenozoic (McArthur et al., 2001, 2020). In~~
156 ~~addition, we used the $\delta^{88/86}\text{Sr}$ record measured in carbonates as a proxy for environmental change~~
157 ~~on the flooded reef platform.~~

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160 2. Materials and methods

161

162 The 86th voyage of the ~~research vessel~~ “Akademik M.A. Lavrentiev” ~~research vessel~~ was
163 held ~~in~~ during July–August 2019. The aim of the expedition was ~~to conduct~~ a comprehensive
164 study of the seamounts of the southern ~~part of the~~ Emperor Seamount Chain. ~~Koko Guyot is the~~
165 ~~southernmost seamount and one of the largest in the Emperor Seamount Chain with a surface~~
166 ~~area of 5,800 km² (Greene et al., 1980). It is located from 34° to 36.5° N and from 170.8° to~~
167 ~~171.5° E. The top of the guyot, located at a depth of 270 m from the sea level (Matter, Gardner,~~
168 ~~1975), is characterize by a predominantly flat upper part at 300–400 m water depth.~~ The subject
169 of ~~this research~~ ~~the present study~~, the southernmost and ~~the~~ youngest seamount of the Emperor
170 Seamount Chain (i.e., Koko Guyot), is an isolated underwater volcanic seamount with a flat top
171 ~~lying~~ more than 300 m below ~~the~~ present ~~mean~~ sea level. ~~‡The guyot-~~ is composed mainly of
172 alkaline ~~basalts with minor and, to a lesser extent,~~ tholeiitic basalts (Clague and Dalrymple,
173 1987). The final stage of eruptions is represented by ~~an interlayering of~~ ~~interlayered~~ pahoehoe

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174 flows, subaerial aa units, and flow foot breccias. ~~In~~ During the course of previous ~~studies, studies~~
175 ~~as part of the~~ Deep Sea Drilling Program (DSDP) and Ocean Drilling Program (ODP), several
176 sediment cores were recovered: DSDP Leg 32 sites 308 and 309 (Shipboard Scientific Party,
177 1975a, 1975b) and ODP Leg 197 Site 1206 (Shipboard Scientific Party, 2002). ~~The studied~~
178 ~~collected material allowed the earliest sedimentation stages and, accordingly, the waning of~~
179 ~~volcanic activity to be investigated. The fossil benthic assemblages, the paleoenvironmental~~
180 ~~setting and the age were also assessed. At the ODP Site 1206, the lava flows are separated by~~
181 ~~limestone and volcanoclastic sandstone layers (Tarduno et al., 2003), which indicate the near-~~
182 ~~surface nature of the eruptions. The materials collected during those expeditions allowed the~~
183 ~~earliest sedimentation stages and waning of volcanic activity to be investigated, as well as fossil~~
184 ~~benthic assemblages, paleoenvironmental setting, and ages volcanic and sedimentary rocks. At~~
185 ~~ODP Site 1206, lava flows are separated by limestone and volcanoclastic sandstone layers~~
186 ~~(Tarduno et al., 2003), suggesting the near-surface nature of the eruptions.~~ The age of the
187 volcanic edifice of the Koko Guyot is estimated ~~to be as~~ about 49–48 Ma (Jackson et al., 1980;
188 Tarduno et al., 2003; Duncan and Keller, 2004). The minimum age of the Koko eruptions ~~is~~ has
189 ~~been~~ determined from nanofossils occurring at the base of the sedimentary cover, which
190 probably overlaps the last lava flow, and coincides with biozones NP14 and NP15 ~~(~~middle
191 Eocene; Speijer et al., 2020). A seismic survey of the Koko Guyot has shown that the volcanic
192 structure is covered by a ~~ea-~~ 600-m-thick carbonate cap associated with coral reef deposits
193 (Davies et al., 1972). The exposed sedimentary part of ~~the section of a~~ drill cores from DSDP
194 sites 308 and 309 is composed of altered volcanoclastic, siltstones and sandstones with a sharp
195 contact between them. The sandstones contain bioclasts, ~~represented of by~~ bryozoans, solitary
196 corals, ostracods, coralline algae, benthic foraminifera, ~~molluses mollusks,~~ and ooids. The fossil
197 assemblage indicates an ~~an early lower~~ Eocene shallow-water setting (Larson et al., 1975).
198 ~~The materials collected for the present study were. The rock material was~~ collected using
199 a remotely operated underwater vehicle (~~of the~~ Comanche type, ~~(~~SUB-Atlantic, UK), equipped
200 with Schilling Robotics Orion hydraulic manipulators, and a Sonardyne hydroacoustic
201 positioning system coupled with a GPS navigation system. During ~~the cruise, the voyage,~~ 11
202 dives were performed to survey the top and slopes of Koko Guyot. Carbonate material was
203 collected during four dives, three of which ~~were located~~ were performed on the northwestern
204 peak of the guyot (dives 4, 8, and 9; Fig. 1) and the fourth in the western part of the main plateau
205 (dive 16; Fig. 1). ~~In addition, a~~ living deep-sea ~~Isidid isidid~~ octocoral, also ~~called termed~~
206 “bamboo coral”, was collected during dive 4. We used ~~this octocoral~~ as a reference ~~of for~~
207 modern carbonate accumulation. Sampling points and physical water characteristics are ~~shown~~
208 ~~presented~~ in Fig. 1 and Table 1. Carbonate rocks were collected directly with a manipulator

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209 ~~operated~~ from the surface (Fig. 2A) and with a 15 ~~cm~~ × 15 cm scoop net (Fig. 2B). ~~In the~~
210 ~~first case~~ For rocks collected by the manipulator, ~~a the~~ rock samples were large enough and a
211 ~~block~~ block measuring 1.5 ~~cm~~ × 1.5 ~~cm~~ × 1.5 cm in size ~~was was~~ cut from the ~~the~~ central part of
212 ~~each~~ each rock sample. These cubes ~~were~~ were passed through a magnet ~~to~~ to remove any metal shavings
213 from the saw and ~~were~~ were washed in distilled water. ~~During the latter operation~~ For material
214 ~~collected by the scoop net,~~ ~~the the~~ sediment was washed with seawater and sorted into different
215 grain-size fractions from 1 ~~mm~~ to 50 mm. After careful visual inspection, the ~~most~~ lightest-
216 colored and unaltered samples devoid of Fe-Mn oxide-hydroxide coatings were selected for
217 geochemical analyses. The selected samples were washed with a brush in running water and
218 finally rinsed in distilled water. All samples were photographed directly on board.

219 Further sample preparation was carried out in the cleanrooms (class 1,000) and laminar
220 boxes (class 100) of the Laboratory ~~o~~ Of Physical ~~a~~ And Chemical Methods ~~o~~ Of Analysis, ~~the~~
221 Zavaritsky Institute of Geology and Geochemistry UB RAS, Ekaterinburg, Russia.

222 Fragments of carbonate rocks without an outer crust and individual parts of fossils
223 weighing about 100 mg were washed three times in ultrapure water (AriumPro, Sartorius). Then,
224 5 ml of 1N HCl were added. ~~Complete~~ Although complete dissolution of all the material ~~was~~
225 ~~observed~~ occurred ~~in~~ during the first few minutes, ~~but~~ the samples were left in the acid for 24
226 ~~hours~~ h at room temperature. ~~Then the~~ The solution was ~~then~~ centrifuged for 20 ~~minutes~~ min at
227 6,000 rpm ~~by~~ in an EBA 21 centrifuge (Hettich, Germany). ~~The resulting, and the~~ supernatant
228 was taken ~~exactly~~ from the central part of the liquid column so ~~that the~~ undissolved residue
229 containing the flakes of ~~possibly~~ possible organic matter would not enter the resulting liquid. ~~The~~
230 ~~following measurements~~ Measurements demonstrated showed that Fe and Mn contents ~~were was~~
231 less than 50 ppm and less than 20 ppm in the majority of the samples, ~~respectively~~. These values
232 ~~are~~ is consistent with ~~the~~ data for the lattice phases of foraminiferal calcite from Palmer (1985)
233 and ~~provide~~ evidenced for the lack of secondary Fe-Mn oxide-hydroxides in the studied
234 solutions. The resulting liquid was divided into two aliquots: 2 ml ~~were was~~ transferred to test
235 tubes for elemental analysis, ~~and~~ the rest of the liquid was ~~left~~ retained for Sr ~~isotopic~~ isotope
236 analysis.

237 An ~~inductively coupled plasma~~ ICP-atomic emission spectrometry (AES) instrument
238 (Optima-8000 DV, PerkinElmer, USA; ~~ICP-AES~~) was used to determine major ~~element~~
239 compositions, ~~such as~~ including Mg, Mn, Sr, and Al, as well as ~~the~~ traces of Fe. ~~The~~ control of
240 the accuracy and precision of ~~determining the major~~ and trace ~~element~~ compositions was
241 ~~carried out~~ performed using IAG/CGL 020 ML-3 certified limestone provided by the Central
242 Geological Laboratory of Mongolia. The ~~concentrations~~ contents of major and trace elements
243 were measured on a regular basis during 2019, yielding the following ~~concentration~~ contents: Fe

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244 $\pm 2350 \pm 350$ ppm, Al $\pm 6000 \pm 900$ ppm, Mn $\pm 180 \pm 30$ ppm, Mg $\pm 8400 \pm 1260$ ppm, and
245 Sr $\pm 1000 \pm 150$ ppm (2SD, N = 30). ~~The o~~Obtained ~~e~~concentration~~conten~~ts were in good
246 agreement with the certified values ~~for of~~ Fe $\pm 2400 \pm 100$ ppm, Al $\pm 6100 \pm 100$ ppm, Mn \pm
247 178 ± 8 ppm, Mg $\pm 8350 \pm 145$ ppm, and Sr $\pm 1018 \pm 30$ ppm (Certificate of analysis IAG /
248 CGL 020 ML-3 (Limestone), 2015)~~(Certificate of analysis..., 2015)~~. The precision of each
249 individual result (relative standard deviation or RSD) ~~during the sample measurement~~ was within
250 better than 1%.

251 The volumes of liquid samples calculated to match ~~e~~~300 ppb of Sr were placed in a
252 PFA vial and evaporated to dryness on a hotplate at 120 °C. ~~Then, the~~The residue was dissolved
253 in 0.5 mL of 7-M HNO₃, placed in an Eppendorf microtube, and centrifuged at 6,000 rpm for 15
254 min by an EBA 21 centrifuge (Hettich, Germany). A sSingle-step chromatography technique
255 using SR-Resin (100–200 mesh, Triskem®, TrisKem International, France) was applied for
256 ~~strontium~~Sr isolation (Vishnevskaya et al., 2020). Purified Sr fraction was evaporated to dryness
257 and dissolved with 3% HNO₃ (v/v) for further isotope ratio measurement.

258 Stable Sr isotopic compositions have been measured in other studies using both TIMS
259 and MC-ICP-MS (McArthur et al., 2020; Teng et al., 2017). ~~The d~~Double-~~spike~~ (DS)
260 technique is usually applied for TIMS (Krabbenhøft et al., 2009; Shalev et al., 2013; Paytan et
261 al., 2021) and MC-ICP-MS (Shalev et al., 2013), although ~~more~~MC-ICP-MS ~~MC-ICP-MS~~
262 analytical protocols have tended to ~~adopted the~~ standard-sample bracketing (SSB) ~~MC-ICP-~~
263 ~~MS~~ MC-ICP-MS (Fietzke and Eisenhauer, 2006; Moynier et al., 2010; Charlier et al., 2012; Ma
264 et al., 2013). ~~Generally~~In general, ~~the~~DS-TIMS is considered to have the highest precision and
265 accuracy, followed by DS-MC-ICP-MS ~~MC-ICP-MS~~ and SSB-MC-ICP-MS ~~MC-ICP-MS~~
266 (Teng et al., 2017).

267 Radiogenic and stable Sr isotopes were measured in this study using an ~~an~~ multicollector-
268 inductively coupled plasma mass spectrometer (~~MC-ICP-MS~~MC-ICP-MS) Neptune Plus
269 instrument (Thermo Fisher Scientific, Germany). The mass bias was corrected using ~~the a~~
270 combination of exponential law normalization ($^{87}\text{Sr}/^{86}\text{Sr} = 8.37861$) and bracketing, with
271 technique (the normalized values ~~were being~~ additionally corrected by the mean reference value
272 of 0.710245 for SRM-987 strontium carbonate (GeoReM database, [http://georem.mpch-](http://georem.mpch-mainz.gwdg.de/)
273 [mainz.gwdg.de/](http://georem.mpch-mainz.gwdg.de/)). ~~In order to control~~To monitor the analytical procedure, SRM-987 was
274 measured on a regular basis, yielding $^{87}\text{Sr}/^{86}\text{Sr} = 0.710261 \pm 0.000020$ (2SD, N = 257). The
275 precision of the determinations ~~method precision~~ estimated as ~~the the~~ within-laboratory standard
276 uncertainty (2σ) obtained for SRM-987 was $\pm 0.003\%$. The precision of each individual result
277 (1 σ SE) during the sample measurement was within better than ± 20 ppm. Long-term analyses of
278 $\delta^{88/86}\text{Sr}$ in SRM-987 processed through chromatographic columns and measured as unknowns

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279 yielded $\delta^{88/86}\text{Sr} = -0.01\% \pm -0.09\%$ (2SD, N = 34). ~~Additionally~~In addition, NIST SRM 1400 bone
280 ash was analyzed as $\delta^{88/86}\text{Sr} = -0.33\% \pm -0.09\%$ (2SD, N = 10), ~~this value was~~ in agreement
281 with ~~that the value~~ provided in the GeoReM database. The precision of each individual result (1 σ
282 SE) ~~during the sample measurement~~ was ~~within better than~~ $\pm 0.006\%$.

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284 3. Results

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286 The studied samples ~~are represented by~~are composed of limestone with a fine-grained
287 matrix (micrite) containing abundant biogenic components (corals, coralline algae, molluscs, ~~and~~
288 benthic foraminifera) and undetermined carbonate fragments. Several samples contain fossil
289 corals, including *Astrea* cf. *amuligera* Milne Edwards & Haime, 1849, *Porites* sp., ~~and~~ at least
290 one other undetermined Merulinidae (Table 2 ~~and~~ Fig. 3). Large benthic foraminifera (LBF)
291 represented by *Spiroclypeus tidoenganensis* Van der Vlerk, 1925 and *Heterostegina* cf.
292 *assilinoidea* (Blanckenhorn) Henson, 1937 occur in ~~samples~~ LV86-9-6, LV86-9-2, and LV86-9-9
293 ~~samples~~ (sample numbers are given ~~in the ascending age order~~ from the oldest to the youngest).
294 ~~Samples~~ LV86-9 and LV86-16 ~~samples~~ consist of cidaroid echinoderm spines (identified by Dr.
295 K.V. Minin, Shirshov Institute of Oceanology of Russian Academy of Sciences; Fig. 3B). The
296 ~~studied samples have a good degree of~~ preservation, ~~degree of the studied samples based on~~
297 ~~assessed by~~ optical examination ~~is good~~.

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298 ~~In general,~~ Under the influence of post-sedimentary fluids, Fe and Mn contents increase
299 and Sr and Mg decrease in carbonates (Veiser, 1983; Banner, 2004; Sawaki et al., 2010).

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300 Consequently, by studying the mutual correlations of these elements, it is possible to ~~select~~
301 ~~identify~~ samples that have been ~~the~~ least affected by diagenetic alteration. ~~In the case~~
302 ~~when~~ ~~Samples with low the chemical composition has not changed, the~~ Mn/Sr ~~and~~ Fe/Sr ratios
303 ~~are are low~~ interpreted as ~~not having undergone~~. We believe that such samples did not undergo
304 diagenetic processes, ~~meaning that their and their~~ isotope characteristics ~~are close to~~ faithfully
305 ~~record~~ those of the primary ~~sedimentary ones~~ materials. ~~The contents of~~ Fe, Mn, Al, Sr, ~~and~~ Mg
306 ~~concentrations~~ in our samples, are very low, except in three samples (Table 3). ~~The~~ Fe/Sr ratio is
307 particularly high in ~~samples~~ LV86-4 and LV86-8-2 ~~samples~~, with values of 0.74 and 0.77,
308 respectively (Table 3). ~~Sample~~ LV86-8-2 ~~sample has also~~ has a high Mn/Sr ratio (0.37), ~~as~~
309 ~~does~~. ~~A high Mn/Sr ratio (0.60) is characteristic of~~ LV86-8-3 (0.60), ~~sample as well~~. These three
310 samples (LV86-4, LV86-8-2, ~~and~~ LV86-8-3), for which at least one of the two ratios (Mn/Sr ~~and~~
311 Fe/Sr) is high, are used with caution in our ~~interpretations~~ analysis, and the isotopic data derived
312 from them are considered less reliable ~~compared with other samples~~.

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313 The Sr isotope composition of two calcified echinoderm spines are very close (0.70917,
314 $\delta^{88/86}\text{Sr}$ 0.24 ‰). LV86-4, LV86-8-2, and LV86-8-3 samples, apparently transformed in the
315 course of secondary processes, have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.708961, 0.708064, and 0.708000,
316 respectively. The Sr isotope composition of the remaining limestones range from 0.70817 to
317 0.70877, with a mean value of 0.70845 (Table 4). Their $\delta^{88/86}\text{Sr}$ varies from 0.09 up to 0.37 ‰
318 with a mean value of 0.22 ‰. An inverse relationship is observed between $\delta^{88/86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$
319 (correlation coefficient*, $C_{\text{cor}} = -0.69$), and a direct relationship between the isotopic
320 composition and Sr content ($C_{\text{cor}} = 0.75$).

321

322 * here and below the equation for calculating the correlation coefficient is:

323
$$\text{Correl}(X, Y) = \frac{\sum (x - \bar{x})(y - \bar{y})}{\sqrt{\sum (x - \bar{x})^2 \sum (y - \bar{y})^2}}$$

324 when \bar{x} and \bar{y} are mean values of two arrays.

325

326 The Sr isotope compositions of two calcified echinoderm spines are very similar
327 ($^{87}\text{Sr}/^{86}\text{Sr} = 0.70917 \pm 0.000008$, $\delta^{88/86}\text{Sr}$ 0.24 \pm 0.01 ‰). Samples LV86-4, LV86-8-2, and
328 LV86-8-3, which we infer to have undergone a degree of diagenetic alteration, have $^{87}\text{Sr}/^{86}\text{Sr}$
329 ratios of 0.708961, 0.708064, and 0.708000, respectively. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the remaining
330 limestones range from 0.70817 to 0.70877, with a mean value of 0.70845 (Table 4), and their
331 $\delta^{88/86}\text{Sr}$ values vary from 0.09 ‰ to 0.37 ‰, with a mean value of 0.22 ‰. An inverse relationship
332 is observed between $\delta^{88/86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ (correlation coefficient, $C_{\text{cor}} = -0.69$, $\rho = 0.13$),
333 meaning that $\delta^{88/86}\text{Sr}$ decreases with decreasing Sr isotopic age. There is a positive relationship
334 between isotopic composition and Sr content ($C_{\text{cor}} = 0.75$, $\rho = 0.08$). Here and below, the
correlation coefficient is calculated as

335
$$\text{Correl}(X, Y) = \frac{\sum (x - \bar{x})(y - \bar{y})}{\sqrt{\sum (x - \bar{x})^2 \sum (y - \bar{y})^2}}$$

336 where \bar{x} and \bar{y} are mean values of two arrays.

337

338 4. Discussion

339

340 4.1. Sr isotope composition: $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{88/86}\text{Sr}$

341

342 The Sr isotope composition of seawater is recorded at the time of formation of for
343 example, carbonate skeletons of marine organisms for example (McArthur et al., 2001; Banner,
344 2004). The Sr isotope composition of ocean water results from the mixing of several Sr sources

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345 with different isotopic signatures (McArthur et al., 2001; Banner, 2004). Terrigenous material of
346 continental origin with a high $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (currently the isotopic composition
347 value of the continental runoff is estimated to be of 0.7116; Palmer and Edmond, 1989) is
348 carried into the ocean basin by rivers, glaciers, and wind. During the weathering of mid-ocean
349 ridge basalts and the halmyrolysis of ocean-floor rocks, Sr with a low $^{87}\text{Sr}/^{86}\text{Sr}$ ratio enters the
350 water (modern value of 0.7037; Palmer and Edmond, 1989). The smallest sources of Sr are
351 marine carbonates, which release upon recrystallization a part of the Sr held in the crystal lattice,
352 which has an average isotopic ratio of 0.7084 (Holland, 1984; De Paolo, 1987; Davis et al.,
353 2003; Banner, 2004). The modern global-ocean value of $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in the World Ocean is
354 0.70917 (Burke et al., 1982; Faure, 1986; Hodell et al., 1989; Banner, 2004; McArthur et al.,
355 2012, 2020).

356 The comparison of the Sr isotope composition of carbonate rocks with the LOWESS
357 global $^{87}\text{Sr}/^{86}\text{Sr}$ variation curve (McArthur et al., 2001, 2012, 2020) makes it possible to
358 determine the age of their formation. At the same time, the ratio of stable ^{88}Sr and ^{86}Sr and
359 ^{88}Sr isotopes (defined as $\delta^{88/86}\text{Sr}$ via with respect to NIST SRM-987 or $\delta^{88/86}\text{Sr}$) in whole,
360 depends on temperature of seawater and species in marine carbonates generally depends on the
361 $\delta^{88/86}\text{Sr}$ value of seawater, which changes through time owing to variations in the same fluxes
362 that control seawater $^{87/86}\text{Sr}$ and the net carbonate flux from the ocean, as well as the degree of
363 fractionation between seawater and carbonate, which depends on species and temperature
364 (Rüggeberg et al., 2008; Krabbenhöft et al., 2010; Vollstaedt et al., 2014; Pearce et al., 2015;
365 Paytan et al., 2021). In the modern ocean, $\delta^{88/86}\text{Sr}$ is 0.378‰ to -0.402‰ (IAPSO standard
366 seawater, http://georem.mpch-mainz.gwdg.de/sample_query.asp). The mineral particles formed
367 in water are characterized by the lower $\delta^{88/86}\text{Sr}$. Moreover, the minerals of chemogenic and
368 biogenic origins can be distinguished by the degree of their stable Sr isotope fractionation
369 (Fietzke and Eisenhauer, 2006; Fruechter et al., 2016). Besides this, the organism behaviour, in
370 particular, the presence of absence of temperature dependence, varies for different species. Thus,
371 belemnites and cold-water corals don't exhibit any temperature dependence (Rüggeberg et al.,
372 2008; Vollstaedt et al., 2014), while $\delta^{88/86}\text{Sr}$ in tropical corals increases with the temperature
373 growth (Fietzke and Eisenhauer, 2006; Rüggeberg et al., 2008), and coccolithophores reveal the
374 inverse temperature relationship (Stevenson et al., 2014). In our work, warm-water species corals
375 had replaced as the dominant species by Larger benthic foraminifera (LBF) and coralline algal,
376 that associated with changes in water depth and temperature. Therefore, we expect that $\delta^{88/86}\text{Sr}$
377 will change with this species transition. However, in this case, it is practically impossible to
378 predict the direction of change (whether $\delta^{88/86}\text{Sr}$ will increase or decrease). Minerals such as
379 carbonate formed in seawater are generally characterized by lower $\delta^{88/86}\text{Sr}$ than seawater because

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380 of seawater–mineral fractionation. Moreover, minerals of chemogenic and biogenic origins can
381 be distinguished by the degree of their stable Sr isotope fractionation (Fietzke and Eisenhauer,
382 2006; Fruchter et al., 2016; AlKhatib and Eisenhauer, 2017; Müller et al., 2018), which depends
383 on temperature and species. Thus, belemnites and cold-water corals do not exhibit temperature
384 dependence of their stable Sr isotope fractionation (Rüggeberg et al., 2008; Vollstaedt et al.,
385 2014), whereas $\delta^{88/86}\text{Sr}$ in tropical corals increases with sea surface temperature (Fietzke and
386 Eisenhauer, 2006; Rüggeberg et al., 2008), and coccolithophores show an inverse temperature
387 relationship (Stevenson et al., 2014). In our study of Koko Guyot, warm-water corals were
388 replaced over time by deeper-water LBF and coralline algae. In our study of Koko Guyot, warm-
389 water corals were replaced over time by deeper-water LBF and coralline algae. Therefore, we
390 expect that $\delta^{88/86}\text{Sr}$ will change over time in association with this species transition/replacement
391 from warm/shallow to cold/deep types. However, in the present study, it is practically impossible
392 to predict the direction of change (i.e., whether $\delta^{88/86}\text{Sr}$ will increase or decrease), due to there
393 are many factors (including sea temperature, sea salinity, and skeleton/shell growth rates) that
394 complicate the interpretation of $\delta^{88/86}\text{Sr}$ measurements.

395 The formation of Koko Guyot occurred about formed at c. -50 Ma (Jackson et al., 1980;
396 Tarduno et al., 2003; Duncan and Keller, 2004), and this is provides a key datum important
397 date for the subsequent discussion belows. The mean $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the echinoid spines
398 analyzed in this study are is 0.70917 \pm 0.00001, which corresponds to the modern isotopic
399 water composition. Taking into account the error of the isotope curve, we can assert that the age
400 of these echinoids is comprised between 50,000 years ago and the present (Fig. 4A). Taking into
401 account the errors associated with the LOWESS global $^{87}\text{Sr}/^{86}\text{Sr}$ variation curve (McArthur et al.,
402 2001, 2012, 2020) we infer that the age of these echinoids is between 50 ka and the present (Fig.
403 4A). The youngest sample of the unaltered limestones used for isotope stratigraphy was is LV86-
404 8-4, which formed yielded an age of 15.30 \pm 0.15 Ma (Langhian, middle Miocene). Limestone
405 sample LV86-9-1 limestone was formed at 18.20 \pm 0.15 Ma, and LV86-9-4 at 19.07 \pm 0.03
406 Ma (Burdigalian, early Miocene). The Sample LV86-9-9, which is composed of the sample with
407 the remains of Merulinidae corals, formed at the Aquitanian–Burdigalian (early Miocene)
408 boundary (20.1 \pm 0.3 Ma), while whereas the limestone sample older LV86-9-2 limestone
409 sample containing *Astrea* cf. *annuligera* is Aquitanian in age (21.65 \pm 0.3 Ma). The oldest
410 studied sample studied, LV86-9-6, is Chattian (Oligocene) in age (25.55 \pm 0.45 Ma). Samples
411 LV86-9-2, LV86-9-6, and LV86-9-9, yielding bearing *Spiroclypeus tidoenganensis* and
412 *Heterostegina* cf. *assilinoidea*, are latest Chattian (Oligocene) to Aquitanian in age. *Spiroclypeus*
413 *tidoenganensis* has been already previously been recognized from the upper Oligocene of Koko
414 Guyot (Hottinger, 1975). Although this species has been reported in from coeval deposits from

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415 [in Saipan \(Hanzawa, 1957\)](#), ~~one cannot rule out~~ its Aquitanian age [is firm](#) (e.g., Hottinger, 1975;
416 Lunt and Allan, 2007). ~~These samples have also mean ages based on Sr isotopes of 21.65, 25.55~~
417 ~~and 20.1 Ma, consistent with the Chattian–Aquitanian age assessed by the larger foraminiferal~~
418 ~~species. Comparison with the curve of $^{87}\text{Sr}/^{86}\text{Sr}$ variations for the altered samples LV86-4,~~
419 ~~LV86-8-2, and LV86-8-3 gives the following ages: 6.7 ± 0.3 , 26.3 ± 0.5 , and 29.2 ± 0.5 Ma,~~
420 ~~respectively. Interestingly, the last two ages are very close to the time of the LV86-9-6~~
421 ~~deposition, and the samples LV86-8-2 and LV86-8-3 may have retained an almost initial~~
422 ~~composition. The three limestone samples LV86-9-2, LV86-9-6, and LV86-9-9 have mean ages~~
423 ~~of 21.65, 25.55, and 20.10 Ma (based on Sr isotopes), respectively, consistent with the Chattian–~~
424 ~~Aquitanian age inferred from LBF species. A comparison with the LOWESS 3 global $^{87}\text{Sr}/^{86}\text{Sr}$~~
425 ~~variation curve (McArthur et al., 2001, 2012) for altered samples LV86-4, LV86-8-2, and LV86-~~
426 ~~8-3 gives ages of 6.7 ± 0.3 , 26.3 ± 0.5 , and 29.2 ± 0.5 Ma, respectively. The last two ages are~~
427 ~~close to the age of LV86-9-6, suggesting that samples LV86-8-2 and LV86-8-3 may have~~
428 ~~approximately retained their initial compositions.~~

429 During the last 35 Ma the $\delta^{88/86}\text{Sr}$ of sea water decreased from 0.38 to 0.30‰ (within
430 $\pm 0.02\%$ analytical error) from 30 to 20 Ma (Paytan et al., 2021; Fig. 4B). Five samples are in
431 this time period. Two of them (Lv 86-8-2, Lv 86-8-3) were probably subject to secondary
432 alterations. It is believed (Voigt et al., 2015) that the $\delta^{88/86}\text{Sr}$ values are more variable in
433 secondary processes. Therefore, for further discussion, we use only those samples that are the
434 least modified. The $\delta^{88/86}\text{Sr}$ value of these samples varies from 0.26 to 0.37‰. Within the margin
435 of error ($\pm 0.09\%$), the results obtained intersect the line of the isotopic composition of water
436 proposed by Paytan et al., (2021). The stable Sr isotope composition of younger samples from 20
437 to 15 Ma (LV86-8-4, LV86-9-1, LV86-9-4) comprising cold water sea species and barren in
438 corals, is rather uniform and average varies near $0.10 \pm 0.03\%$. The change in the temperature and
439 light regime led to the biocommunity alteration, in our case, reef benthic assemblages were
440 replaced as the dominant species to larger foraminiferal species. We suppose that it is expressed
441 in the dramatic decrease of $\delta^{88/86}\text{Sr}$ (Fig. 4). Biocommunity alteration to much more cool water
442 resistance can be correlated with the bottom subsidence rate and guyot migration to higher
443 latitudes (Wilson, 1963; Clague and Dalrymple, 1987; Tarduno et al., 2003; Clague et al., 2010).
444 The $\delta^{88/86}\text{Sr}$ values of modern echinoids are also less than $\delta^{88/86}\text{Sr}$ curve. It is probably that Sr
445 isotope fractionation between cold water species and water is much stronger than between warm
446 water species and surrounding water. However, the last statement requires additional research
447 and is beyond the scope of this study. From 30 to 20 Ma, the $\delta^{88/86}\text{Sr}$ of seawater decreased from
448 0.38‰ to 0.30‰ (within $\pm 0.02\%$ analytical error) (Paytan et al., 2021; Fig. 4B). Five of the
449 studied samples have ages within this time interval. Two of these samples (LV86-8-2 and LV86-

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450 8-3) have probably been affected by diagenetic alteration. Because diagenetic processes have
451 been shown to alter the initial $\delta^{88/86}\text{Sr}$ of carbonates (Voigt et al., 2015), we use only the three
452 least modified samples as a basis for our discussion. The $\delta^{88/86}\text{Sr}$ value of these samples varies
453 from 0.26‰ to 0.37‰. Within the margin of error ($\pm 0.09\%$), the results obtained intersect the
454 line indicating the isotopic composition of seawater proposed by Paytan et al. (2021). The stable
455 Sr isotope composition of younger samples from 20 to 15 Ma (LV86-8-4, LV86-9-1, and LV86-
456 9-4) comprising cold-water sea species and lacking corals is rather uniform, with the mean
457 $\delta^{88/86}\text{Sr}$ varying within $0.10\% \pm 0.03\%$. These values are much lower than the isotope curve
458 proposed by Paytan et al. (2021) (Fig. 4B). The $\delta^{88/86}\text{Sr}$ values of modern echinoids are also
459 lower than (although within measurement errors of) the $\delta^{88/86}\text{Sr}$ curve.

460 It has been shown that carbonates have lower $\delta^{88/86}\text{Sr}$ values than the sedimentation
461 medium, and the difference can be more than 0.1‰ (Raddatz et al., 2013, Vollstaedt et al.,
462 2014). Kisakürek et al. (2011) and Böhm et al. (2013) explained this disparity by calcification in
463 a largely open system at high precipitation rates. The shift to a benthic community that is more
464 resistant to colder water can be correlated with bottom subsidence and guyot migration to higher
465 latitudes (Wilson, 1963; Clague and Dalrymple, 1987; Tarduno et al., 2003; Clague et al., 2010).
466 The change in temperature and light regime at Koko Guyot as it subsided and migrated to higher
467 latitudes led to a change in the benthic community as reef benthic assemblages were replaced by
468 those dominated by LBF (and coralline algae). The change in temperature and light regime at
469 Koko Guyot as it subsided and migrated to higher latitudes led to a change in the benthic
470 community as reef assemblages were replaced by those dominated by LBF and coralline
471 algae. We presume that this change in benthic community is recorded as a sharp decrease in
472 $\delta^{88/86}\text{Sr}$ values in our samples compared to sea water (Fig. 4B) without major changes in
473 seawater $\delta^{88/86}\text{Sr}$ values. It is probable that Sr isotope fractionation between cold-water species
474 and ambient seawater is much stronger than that between warm-water species and ambient
475 seawater. However, we cannot take into account temperature and depth changes in this paper.

476

477 4.2. Rate of subsidence of Koko Guyot and its variation over timeSubsidence rates

478

479 Grigg (1988) identified corals *Favites* sp., *Platygyra* sp., *Psammocora* (*Stephanaria*) sp.,
480 and *Seriatopora* sp. from Koko Seamount, the ages of which ranged from 30.5 to 24.7 Ma, via-as
481 determined using Sr isotope stratigraphy. Clague et al. (2010) obtained ages for corals ranging
482 from 50 to 27 Ma, whereas-compared with 16 Ma for LBF 46 Ma, on the basis of which those
483 authors. Discussing these data, Clague et al. (2010) calculated the subsidence rate of the volcano
484 to be as 0.012 ± 0.003 mm/yr. Previously-Davies et al. (1972) based-on-used water depth, guyot

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485 structure, and the age and species composition of corals ~~to~~ estimated the subsidence rate of
486 Koko Guyot ~~at as 42 m/Ma or~~ 0.042 mm/yr throughout the existence of the guyot.

487 Our ~~method of estimation~~ estimation of subsidence rates for Koko Guyot ~~subsidence rate~~
488 ~~follows these~~ incorporated the following assumptions: (1) reef formation slowed ~~down~~ and then
489 stopped ~~due owing~~ to submersion below the euphotic zone, ~~the which is the~~ lower depth limit of
490 coral and algal growth; (2) the identified fossil benthic assemblage from the guyot's plateau
491 lived in optimal ~~conditions of~~ depth (i.e., 0–30 m) and temperature (average winter water
492 temperature >18 °C) conditions for reef growth (Veron, 1995); ~~and~~ (3) later benthic
493 communities, devoid of reef corals, lived at greater water depths >30 m. Warm-water corals
494 grow at a certain depth, no more than 30 m (Veron, 1995). As the seafloor subsides and relative
495 sea-level rise resultantly occurs, the reef ~~buildup grows~~ builds up vertically to retain a the
496 "comfortable life"-zone of maximum favorability for coral existences. We took the maximum
497 water depth of this zone for ~~such~~ corals in this study at as 30 m. We also ~~decided~~ assumed that
498 the formation of the carbonate skeleton occureds under normal conditions. With ~~the~~ gradual
499 subsidence of the seafloor, we assumed that the reef of Koko Guyot was able to keep up with
500 sea-level rise as so long as the seafloor was within the euphotic zone. As the rate of sinking
501 increaseds, new colonies will would have formed faster more quickly to grow to a comfortable
502 favorable depth (maximum 30 m). ~~Thus, samples with a small difference in age will occur more~~
503 ~~often. Proceeding from the sample ages obtained, we plotted the curve of the coral age versus the~~
504 ~~age difference (Fig. 5). It can be seen from the graph that the age difference between the samples~~
505 ~~at the early stage of "guyot life" is smaller, and this difference increases with age. This suggests~~
506 ~~that the rate of reef growth, or volcano's subsidence, was irregular. With a high subsidence rate,~~
507 ~~the coral growth rate will also be faster. The «new» corals will record the «new» isotopic~~
508 ~~composition of water. Thus, samples with a small difference in age will occur more often. Thus,~~
509 ~~we have described our «model object» and proceed to the calculations.~~

510 We took all age estimates (Grigg, 1988; Clague et al., 2010; this work), ranked them from
511 ~~minimum youngest to maximum oldest~~, and calculated the difference between each successive
512 age (~~difference ranged which ranged from from~~ 0 to 2 Myr), ~~thus~~. ~~As a result, we obtain~~ ing 26
513 ~~points datapoints~~ (Table 5 ~~and~~; Fig. 5), Figure 5 shows that the age difference between the
514 samples during the early stage of guyot evolution is small and that this difference increases with
515 Koko Guyot age. The pattern of data in Fig. 5 suggests that the rate of reef growth (or of the
516 guyot's subsidence) varied over time. The age difference ~~over for~~ the period 30–25 Ma is smaller
517 than ~~that during for the period~~ 25–15 Ma, suggesting that the reef grew faster more quickly
518 during the older period. The age of the youngest identified coral specimen is 20.1 ± 0.3 Ma
519 (LV86-9-9). This sample may, therefore, mark the last-final episode of active reef growth, after

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520 which the platform ~~was more deepened~~deepened to a position and located below the euphotic
521 zone ~~where corals can thrive due to the subsidence of the guyot~~ (Wilson, 1963; Clague and
522 Dalrymple, 1987; Tarduno et al., 2003; Clague et al., 2010). ~~Moreover, we~~We also sampled a
523 coralline algal crust dated at 15 Ma (LV86-8-4). The sample was collected from a depth of 1-458
524 m, where it ~~laid was located~~ in a soft (unconsolidated) substrate. ~~This sample~~ most likely slid
525 down the slope from the nearest plateau, whose ~~current top is today at height is at~~ 350 m water
526 depth. Assuming a maximum water depth of 120 m for the living coralline algae and 30 m for
527 the living youngest zooxanthellate corals sampled (Clague et al., 2010), we ~~have calculated that~~
528 ~~the following:~~ (1) ~~From or the last~~ 15 Ma to the present, Koko Guyot subsided at a ~~speed rate of~~
529 ~~(350 - 120)/15.3 = 15.0 m/Myr, that is, (i.e., 0.015 ± 0.002 mm/yr);~~ and (2) ~~in during the~~
530 period from 20 to 15 Ma, the ~~average mean~~ subsidence rate was ~~(120 - 30)/(20.1 - 15.3) =~~
531 ~~18.8 m/Myr, that is, 0.019 ± 0.003 mm/yr. Previous studies~~A previous study ~~suggest has~~
532 ~~suggested~~ that the ~~very first initial~~ shallow-water sediments formed ~~in during~~ the period ~~from~~
533 ~~from 49.7 to 43.5 Ma, which was found as identified~~ in the ODP Site 1206 (Fig. 1) core
534 recovered at 1500 m water depth (Shipboard Scientific Party, 2002). The bottom of this layer
535 was 57 m from the top of the column (Shipboard Scientific Party, 2002; Tarduno et al., 2003).
536 Thus, ~~if we applying~~ our calculation method, the subsidence rate ~~in during~~ the first tens of
537 million years ~~(from 49.7 to 43.5 Ma)~~ is estimated as ~~st approximately~~ 0.046 ± 0.005 mm/yr
538 ~~[using (as the average of 49.7 and 43.5 Ma is 46.6 Ma, we calculate the subsidence rate as~~
539 ~~follows: (1500 + 57 - 350)/(46.6 - 20.1) = 46.2) m/Myr or 0.046 ± 0.005 mm/yr, where 46.6~~
540 ~~Ma is the mean of 49.7 and 43.5 Ma]~~ (Fig. 6), which ~~was is~~ close to the rate reported by Davies
541 et al. (1972). ~~Our calculations showed that the~~Our ~~calculated~~ average subsidence rate ~~was is~~
542 ~~slightly higher than that suggested estimated~~ by Clague et al. (2010) ~~of, i.e. 0.008–0.012 mm/yr~~
543 ~~over since last 23 Ma yr. Our~~However, our results are consistent with ~~other observations that the~~
544 ~~observation that~~ the subsidence rate of the ocean floor decreases as the age of the ocean crust
545 increases ~~(for example, e.g.,~~ Sclater et al., 1980; Marty and Cazenave, 1989; Stein and Stein,
546 1992). This process represents ~~the~~ seafloor flattening, meaning that old seafloor is shallower than
547 ~~that~~ predicted by the “root-t” model (i.e., a linear increase in ocean depth with increasing crustal
548 age; Parsons and Sclater, 1977; Hillier, 2010).

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5. Conclusions

552
553 The study of Sr isotope composition showed that the least altered limestones containing
554 the fragments of reef corals were formed in the early Miocene. No coral fragments were found in

555 older samples (Late-Oligocene). A study of the distribution of stable strontium isotopes in warm-
556 water marine organisms and cold-water ones showed that the fractionation of stable strontium
557 isotopes between cold-water species and water is probably higher than between warm-water ones
558 and water. We investigated the Sr isotope compositions of Oligocene–Miocene coral reef
559 limestone from Koko Guyot in the southern Emperor Seamount Chain to assess the dynamics of
560 the subsidence of this guyot. Our study of Sr isotope compositions ($^{87}\text{Sr}/^{86}\text{Sr}$) showed that the
561 least altered limestones containing fragments of reef corals were formed during the early
562 Miocene. No coral fragments were found in older samples (late Oligocene). Analysis of the
563 distribution of stable Sr isotopes ($\delta^{88/86}\text{Sr}$) in warm-water sediments showed a low degree of
564 fractionation compared with seawater. The $\delta^{88/86}\text{Sr}$ values of cold-water species, which replaced
565 warm-water species at around 20 Ma, differ significantly from the seawater $\delta^{88/86}\text{Sr}$ variation
566 curve estimated by Paytan et al. (2021).

567 Using several independent methods, we confirm the change in environmental parameters
568 and determine the time limit of this change about 20 Ma. The same boundary corresponds to a
569 change in the rate of subsidence. From about 49–44 Ma to 20 Ma the subsidence rate of Koko
570 Guyot was 0.046 ± 0.005 mm/yr. The $\delta^{88/86}\text{Sr}$ values of coral samples, that formed 25–20 Ma,
571 varies from 0.26 to 0.37 (± 0.09)‰ and these values are consistent with the variation curve
572 proposed by Paytan et al., (2021). At the lower limit of this period, the biocommunity was re-
573 adjusted due to the fact that the surrounding waters became colder. Warm-water corals
574 disappeared and were replaced by Larger benthic foraminifera and coralline algal. From 20 to 15
575 Ma ago, the subsidence rate was lower more than twice, 0.019 ± 0.003 mm/yr. The $\delta^{88/86}\text{Sr}$ values
576 of this samples are about 0.10‰. Finally, in the last 15 Ma the volcanic structure has been
577 subsided at a rate of 0.015 ± 0.002 mm/yr. The data obtained refine the existing models of
578 subsidence of the Pacific crust. Understanding the differential rate of subsidence is important
579 insofar as it supports the model of ocean floor cooling after the Pacific plate passed over the
580 stationary mantle hotspot, which may be particularly important insofar as the seamount sits at the
581 junction of plate rotation as seen from the different trajectory of the Emperor and Hawaiian
582 chains. Using several independent methods, we confirmed a change in environmental parameters
583 at around 20 Ma. This timing also corresponds to a change in the rate of subsidence. From 49–44
584 to 20 Ma, the subsidence rate of Koko Guyot was 0.046 ± 0.005 mm/yr. The $\delta^{88/86}\text{Sr}$ values of
585 coral samples that formed from 25 to 20 Ma vary from 0.26‰ to 0.37‰ (± 0.09)‰ and are
586 consistent with the variation curve proposed by Paytan et al. (2021). At the ending of this period,
587 the benthic community changed because of cooling ambient waters. Warm-water corals
588 disappeared and were replaced by LBF and coralline algae. From 20 to 15 Ma, the subsidence
589 rate was much lower at 0.019 ± 0.003 mm/yr. The $\delta^{88/86}\text{Sr}$ values for samples that formed during

590 this period are ~0.10%. Since 15 Ma, the volcanic structure has subsided at a rate of 0.015 ±
591 0.002 mm/yr. The data obtained in this study refine existing models of the crustal subsidence of
592 the floor of the Pacific Ocean, which suggest a constant rate of seafloor subsidence.
593 Understanding the changing rate of subsidence is important because it is related to the process of
594 ocean-floor cooling after the Pacific Plate passed over the mantle Hawaiian hotspot.

596 **Declaration of competing interests**

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626

627 Data availability

628 All data ~~is~~are provided in attached files and ~~at on~~
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830 Figure and table captions

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832 Fig. 1. (A) ~~A~~ Geographic map of the Hawaiian–Emperor bend. (B) ~~B~~ Bathymetric map of
833 Koko Guyot ~~bathymetric map~~. ~~P~~ points represent sampling sites for dives 4, 8, 9, and 16. Deep
834 Sea Drilling Project sites 308 and 309 and Ocean Drilling Program Site 1206 are shown ~~by~~
835 ~~value~~. The ~~s~~Source of the bathymetric map is <http://earthref.org>.

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837 Fig. 2. ~~Photographs of s~~Sampling conducted by a ~~Comanche~~ remotely operated underwater
838 vehicle ~~of the Comanche type~~: (A) ~~R~~ock sampling ~~with a manipulator~~ from the plateau of the
839 guyot ~~using a manipulator~~ (dive 9; sample Lv86-9-2); (B) ~~with Sampling using~~ a scoop net
840 mounted on the manipulator (dive 9; ~~s~~ample Lv86-9 echinoid).

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842 Fig. 3. (A) ~~A~~ Modern octocoral of the ~~family~~ Isididae ~~family~~ (sample Coral). (B) ~~E~~chinoderm
843 spines (Cidaroida; sample LV86-9 echinoid). (C–D) ~~L~~arger ~~foraminiferal~~ packstone with
844 *Spiroclypeus tidoenganensis* (*St*) and *Heterostegina* cf. *assilinoidea* (*Ha*) (samples Lv86-9-2 ~~and~~
845 Lv86-9-6). (E) ~~R~~eef coral *Astrea* cf. *annuligera* (sample Lv86-9-2; i, thickened costo-septum;
846 ii, paliform lobe). (F–G) ~~B~~ioclastic packstone showing (F) the ~~encrusting~~ coralline
847 *Lithoporella* sp. with two uniporate conceptacles (arrows; sample LV86-8-3; conc., conceptacle);
848 and (G) bryozoans (bry) and coralline fragments (cor; sample LV86-9-4).

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850 Fig. 4. Comparison of the Sr isotopic composition of the studied samples with (A) ~~the~~
851 ~~r~~adiogenic Sr isotope record (LOWESS 5; McArthur et al., 2012) and (B) ~~a~~ model of ~~the~~ stable
852 Sr isotope record with $\pm 0.02\%$ analytical uncertainty (~~grey area~~; Paytan et al., 2021) in the
853 ocean. Crossed-out circles ~~are represent data from~~ diagenetically altered samples. ~~E~~ error bars ~~at~~
854 ~~the level of are~~ $\pm 0.09\%$.

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856 Fig. 5. Relationship between age and age difference between two consecutive ages for carbonate
857 samples. The difference between the ages of ~~the consecutive~~ older samples is less than that of the
858 younger ~~ones~~ samples. This suggests that the rate of ~~subsidence of the~~ reef superstructure ~~is~~
859 ~~ancient times was initially high~~ ~~was higher than afterwards~~ and ~~subsequently decreased~~ (i.e., the
860 subsidence rate was higher when ~~the~~ coral reef and the guyot were younger). Data from this

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861 work (circles), Grigg (1988; diamonds), and Clague et al. (2010; squares) are plotted in the
862 ~~graph figure~~.

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864 Fig. 6. Schematic model for the vertical motions of Koko Guyot. The bold line in the graph
865 shows the changing position of the summit of the volcano, which formed at 49–48 Ma (Jackson
866 et al., 1980; Tarduno et al., 2003; Duncan and Keller, 2004). The numbers in the figure rates
867 given in the figure indicate the subsidence rate, calculated according to the assumptions adopted
868 in the text using the method presented in Section 4.2.

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869

870 Table 1. Coordinates and water depths of samples ~~analysed~~ analyzed in this study, and seawater
871 temperature and salinity at the sampling sites.

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872 T, water temperature; S, salinity; Coral, sample of modern ~~Isididae~~ isididae coral; echinoid,
873 sample of echinoid spines.

874

875 Table 2. Lithology and biotic components of the studied Koko Guyot carbonate samples.

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877 Table 3. Trace ~~element~~ contents and calculated Fe/Sr and Mn/Sr ratios ~~in~~ of the studied
878 carbonates. ~~The analysis was were carried out by~~ performed using the ICP–AES. C, and the
879 eontents are given in ppm.

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880

881 Table 4. Strontium isotope compositions and ages according to LOWESS 5 (McArthur et al.,
882 2001, 2012).

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883

884 Table 5. Strontium isotope ages of samples from the present study and previous studies (blue,
885 Grigg, 1988; yellow, Tarduno et al., 2003; green, Clague et al., 2010; white, this work study)
886 used to calculate age differences between consecutive samples.