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Lead profiles in red coral skeletons as high resolution records of pollution in the Mediterranean Sea

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Abstract

Lead concentrations in long-lived *Corallium* species of known age, from the Mediterranean Sea, Atlantic and Pacific Oceans, were determined by laser ablation, inductively coupled plasma mass spectrometer (LA-ICPMS). Lead concentrations in a 2000-year-old sub-fossil Mediterranean *C. rubrum* are ca $0.09 \pm 0.03 \mu\text{g/g}$. For the period 1894-1955, lead concentrations in *C. rubrum* skeletons from the Mediterranean are stable within the range 0.2-0.4 $\mu\text{g/g}$; concentrations increase to about 1-1.2 $\mu\text{g/g}$ during the period 1960-1978, then decrease progressively to stabilize and reach values in the range 0.2-0.4 $\mu\text{g/g}$ in present-day corals. These variations can be related to the lead gasoline pollution event that (1) started in the early 1950s with the increase of the numbers of cars in the world, and (2) was mitigated by the implementation of new regulations starting in 1975, leading to a return to pre-1950 levels in 2000. In the Pacific, lead concentrations in *C. japonicum* and *C. konojoi* are lower than in the Mediterranean *C. rubrum*, with values close to $0.17 \pm 0.03 \mu\text{g/g}$. The lowest lead concentrations in present-day samples ($0.11 \mu\text{g/g}$) are found in *C. johnsoni* and *C. niobe* from the Azores islands in the Atlantic, and in a Mediterranean *C. rubrum* from Montecristo Island, one of the least accessible and most protected areas in the Mediterranean Sea. Using lead concentrations in *C. rubrum* and in the Mediterranean seawaters, a partition coefficient $K_d = [Pb/Ca]_{\text{calcite}} / [Pb/Ca]_{\text{seawater}}$ of 13 ± 3 is estimated; it allows calculating past and present lead contents in seawater in which corals grew. Application to *Corallium* species indicates that values endangering human health or threatening the preservation of aquatic ecosystem on long terms were nearly reached or exceeded in Mediterranean seawaters at the maximum of the lead gasoline pollution event in the 1980s. Measurements in *C. rubrum* from different places in the Mediterranean indicate that present-day seawater concentrations vary between

49 40 and 200 pmol/kg. As expected, the lowest concentrations come from protected areas
50 insulated from human activities, while the highest come from places close to lead mining or
51 processing sites.

52 **Keywords**

53 Lead, *Corallium*, Calcite, Seawater, Partition coefficient, Diagenesis, Sciacca

54 **Highlights**

55 - Lead contents in *Corallium* skeletons record the lead gasoline pollution event (1950-2000)

56 - Lead contents are lower in Atlantic and Pacific corals than in the Mediterranean

57 - Levels endangering the preservation of aquatic ecosystems were reached in the 1980s

58 - Lead contents in present-day Mediterranean corals returned to pre-1950 levels

59

60 1. Introduction

61 Biominerals have been used routinely as proxies of environmental conditions through
62 compositions in major, minor, trace elements and isotopes [e.g. Chave (1954); Epstein and
63 Lowenstam (1953)]. Among biominerals, biogenic calcium carbonates are able to incorporate
64 different elements in significant amounts. In the case of *Corallium* species, these include
65 magnesium, strontium, sodium, sulfur, lithium, barium, lead and uranium [see Vielzeuf et al.
66 (2018); Vielzeuf et al. (2013) for summaries]. However the ability to incorporate an element
67 is not a guarantee of a faithful environmental proxy as concentration variations can also be
68 due to biological or physico-chemical effects, or combinations of factors. Thus, the potential
69 of each element as a proxy in a given species has to be tested. The precious red coral
70 *Corallium rubrum* (*Cnidaria*, *Anthozoa*, *Octocorallia*) is an emblematic species of the
71 western Mediterranean but is also present in the Atlantic Ocean along the southern coast of
72 Portugal, and along the coast of Morocco (Zibrowius et al., 1984). The red coral grows within
73 a large range of depths from near-surface down to ~1000 m (Costantini et al., 2010; Knittweis
74 et al., 2016). This colonial organism has a ramified erect growth-form and a skeleton made of
75 high magnesian calcite (Lacaze-Duthiers, 1864). Its skeleton has a slow radial growth of

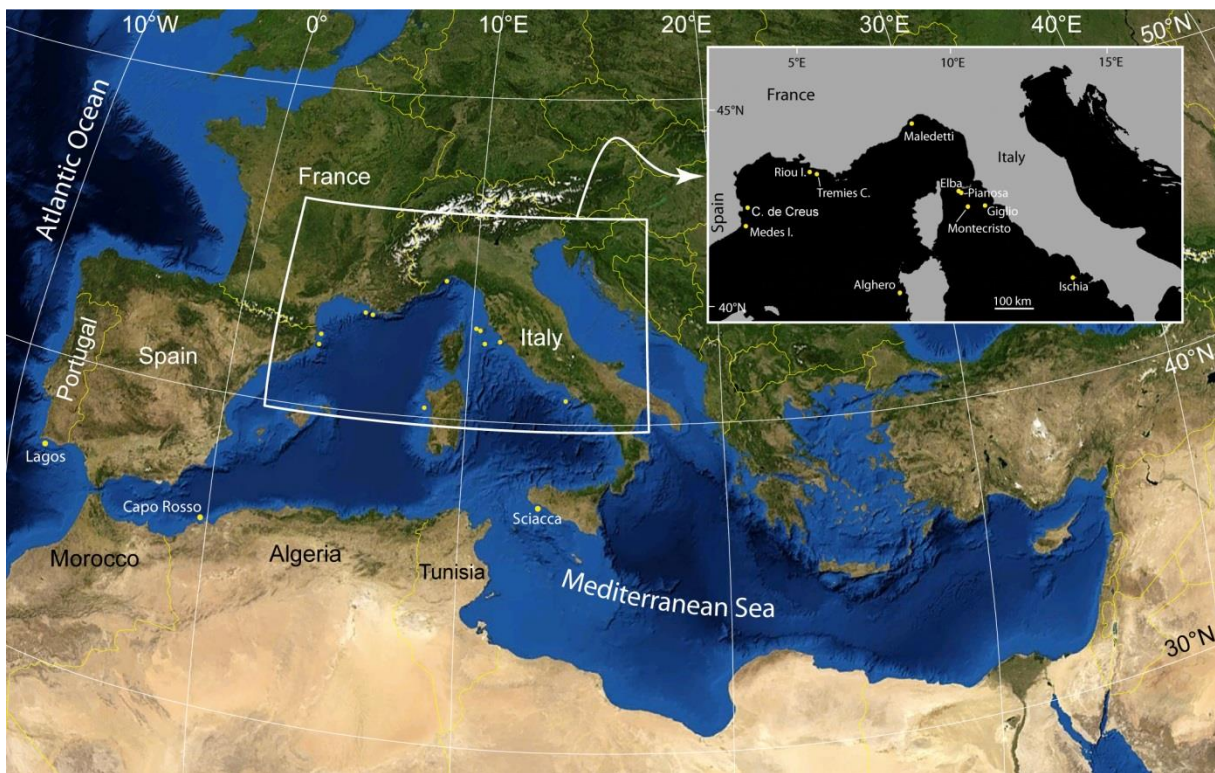
76 about 100 to 200 μm per year (Marschal et al., 2004) and can live several decades (Garrabou
77 and Harmelin, 2002). In a companion paper, it has been determined that growth kinetics plays
78 a role in the incorporation of Mg, Na, Sr, Li, S and U in the skeletons of *Corallium* species
79 (Vielzeuf et al., 2018). Conversely, it was shown that growth kinetics does not influence the
80 incorporation of Ba and Pb. Concerning lead, large variations of concentrations in corals were
81 observed (Vielzeuf et al., 2018). These data raised the question of the origin and significance
82 of the variations of lead in *Corallium* skeletons. It is a well-known fact that human activities
83 resulted in massive release of lead into the earth surface (Boutron et al., 2004; Patterson,
84 1965; Wu and Boyle, 1997). Paleo-environmental and archaeological records suggest that
85 lead pollution started as early as the Chalcolithic (~5000 cal. Yr. BP) (Martinez-Cortizas et
86 al., 1997; Martinez Cortizas et al., 2016; Settle and Patterson, 1980). Most importantly, the
87 use of lead additives in gasoline initiated in 1923 created a public health problem worldwide
88 (Patterson, 1965). In this study, we determine the lead concentrations in the skeletons of
89 *Corallium* species by LA-ICPMS and discuss the incorporation of lead in biogenic high
90 magnesian calcites. The question whether the lead content in red coral skeletons is a potential
91 proxy of the concentration of lead in the Mediterranean Sea is also addressed. Concentration
92 profiles at annual-scale resolution are obtained in *C. rubrum* skeletons of different ages and
93 provenances. The discussion is extended toward *Corallium* species from the Atlantic (*C.*
94 *rubrum*, *C. niobe* and *C. johnsoni*) and the Pacific (*C. japonicum* and *C. konojoi*). Finally, the
95 results are compared to other lead records in the Mediterranean basin, in the Atlantic and
96 Pacific Oceans, and in polar ice cores.

97 2. Material and methods

98 2.1. Samples

99 2.1.1 *C. rubrum*

100 *Present day C. rubrum* - Analytical profiles were mainly performed on five modern colonies
101 of *C. rubrum* with known place and date of sampling. The colonies were collected (i) at Riou
102 Island (Marseille, France) in 2002, (ii) in the Calanques area near Cassis (France), in a 15 m
103 depth marine cave (the Tremies cave) in 2010, (iii) near the Medes Islands (L'Estartit, Spain)
104 in 2002 and 2014, and (iv) near Cap de Creus (Spain) in 1962. **Figure 1** shows a map with the
105 original locations of the colonies. Samples were collected at depths varying between 15 m and
106 73 m, i.e. in the range of surface waters.



107
108 **Figure 1:** Map of the north-western Mediterranean Sea with locations of the studied samples.

109 Additional LA-ICPMS analyses (not necessarily along analytical traverses) were
110 carried out on recent colonies from Algeria and Italy (including Montecristo island), to
111 enlarge our vision of lead contents in the Mediterranean (Table 1 – supplementary materials).

112 *Sub-fossil C. rubrum* samples – A sub-fossil sample of *C. rubrum* skeleton buried in the
113 sediments of the Tremies Cave was collected in 2007. Its absolute age was determined as
114 1950 ± 30 years BP by ^{14}C dating in the Poznań Radiocarbon Laboratory.

115 Quite surprisingly, huge amounts of red coral collected in Italy in the last 150 years
116 came from the sub-fossil coral reservoir of the Sciacca Banks (Sicily Channel) where 18,000
117 tons were collected in 34 years (Cattaneo-Vietti et al., 2016; Rajola, 2012). Large
118 uncertainties still exist on the age of these sub-fossil colonies, but four samples were carbon
119 dated at University of Salento (Italy) and provided ages between 2000 and 10,000 years BP
120 (Rajola, 2012). In this study, we present LA-ICPMS data on a Sciacca sub-fossil sample
121 whose age has not been determined, but is assumed to be in the range 2,000-10,000 years BP.

122 Independently from the analyses carried out in France, other present-day
123 Mediterranean *C. rubrum* samples from Spain, Italy, North Africa, and sub-fossil Sciacca
124 corals (Sicily, Italy) were analyzed at Virginia Tech. (USA) and these data will be presented
125 and discussed here. Two samples of the Sciacca corals were dated by radiocarbon and gave
126 ages of 2400-2100 years BP and 4400-4050 years BP (Rajola, 2012).

127 *C. rubrum from the Atlantic* - In Portugal, coral fisheries were abandoned about 300 years ago
128 (Zibrowius et al., 1984). Recently, *C. rubrum* colonies were re-discovered in Southern
129 Portugal (Boavida et al., 2016). Two rare samples from Sagres (Lagos Portimão) collected at
130 90m depth (Boavida et al., 2016) were also studied by LA-ICPMS.

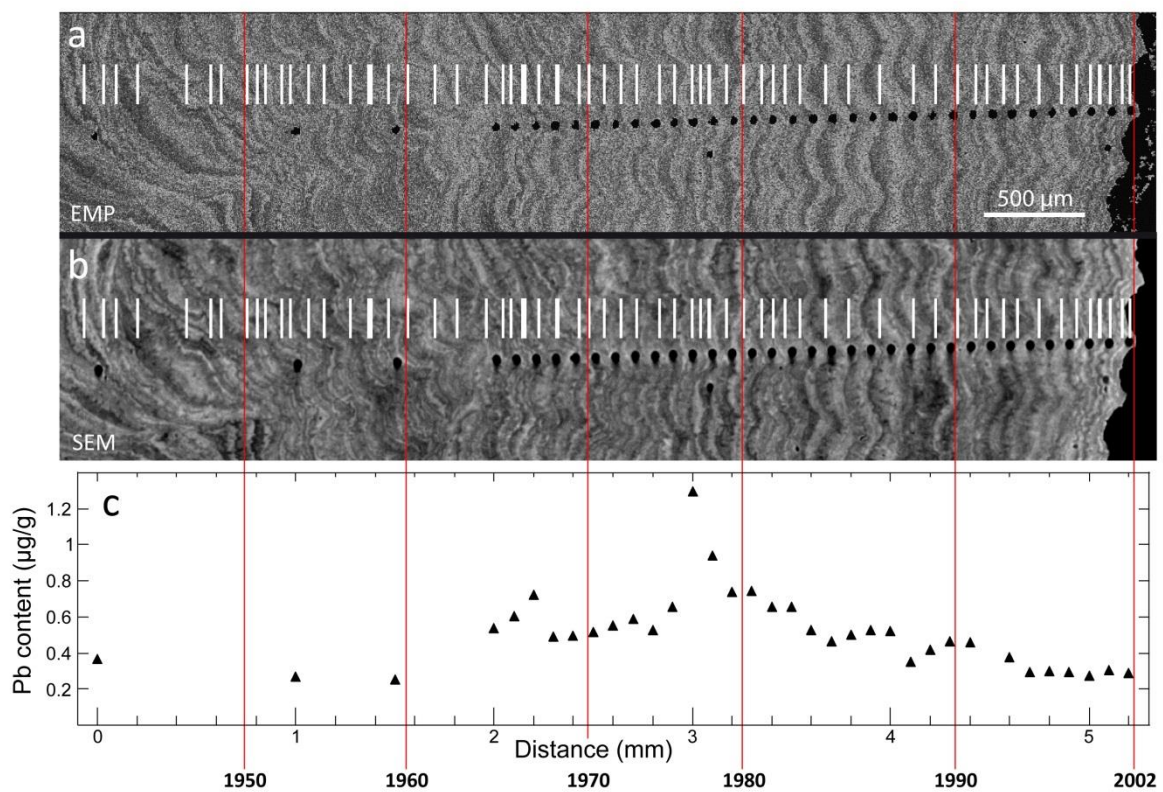
131 2.1.2 - Other *Coralliidae*

132 Skeletons of *Corallium niobe* and *C. johnsoni* from the Atlantic (Azores Islands) have been
133 collected in 2005 and 2011, respectively, and two specimens of *Corallium* species from the
134 Pacific (*C. japonicum* and *C. konojoi*) have been harvested along the Japan coast in 2013 and
135 2015, respectively.

136 Geographic locations, depths and sampling dates of all samples are given as
137 supplementary materials in Table 1, and in Vielzeuf et al 2018 (supplementary materials,
138 Table 1).

139 2.2 Preparation of the samples, growth rings identification, and age determination

140 Contrary to banded scleractinian corals made of aragonite, *Corallium* species have dense
 141 skeletons without marked porosity. For this reason and because of the selected analytical
 142 technique (LA-ICPMS), no cleaning preparative sequence of the samples was necessary, as is
 143 the case for scleractinian corals [e.g. Shen and Boyle (1988)]. For each colony, one or two
 144 branches were cut transversally, mounted in epoxy, and polished with diamond paste down to
 145 0.25 μm .



146

147 **Figure 2:** EMP Mg map and SEM images. a) Electron microprobe map of magnesium and
 148 LA-ICPMS profile in a sample collected near the Medes Islands in 2002. The contrast has
 149 been inverted for a better comparison with the SEM image (bright to dark – low to high Mg
 150 contents). The white vertical lines mark each annual growth ring. The black dots (40 μm in
 151 diameter) are the locations of the LA-ICPMS analyses. b) Mosaic of SEM images of the same
 152 area. c) Pb concentrations obtained in the LA-ICPMS profile (see figure 4 for other profiles).

153

154 It has long been known that *C. rubrum* skeletons display growth rings (Lacaze-
 155 Duthiers, 1864). By surveying colonies over long periods of time, Garrabou and Harmelin
 156 (2002) determined the axial (height) and radial (diameter) growth rates of *C. rubrum* colonies

157 as 1.8 mm and 0.25 mm year⁻¹, respectively. Concomitantly, Marschal et al. (2004) developed
158 a method to identify growth rings by staining the organic matrix. Annual growth rings are
159 about 100 to 200 µm thick (Marschal et al., 2004). These authors demonstrated the annual
160 periodicity of the growth rings by *in situ* calcein labeling of some colonies. Then, it was
161 demonstrated that growth rings are also marked by variations of magnesium (Vielzeuf et al.,
162 2008; Vielzeuf et al., 2013). These variations can be detected by electron microprobe (EMP)
163 mapping, but also by scanning electron microscopy (SEM) using backscattered electron
164 (BSE) imaging. Mg-rich rings appear darker than Ca-rich rings in SEM BSE images because
165 Mg has a lower atomic number (Z) than Ca. The exact correlation between Mg-rich rings
166 observed by electron probe and dark rings in BSE images can be observed in [Figure 2a](#) and
167 [2b](#). Note that in EMP maps low concentrations normally appear in black. However, for a
168 better comparison of EMP and SEM images, the contrast of the EMP image was inverted in
169 [Fig. 2](#) (dark layers indicate high concentrations of Mg). In the present study, SEM was the
170 main method used to image the growth rings because of its non-destructive character
171 (contrary to OM staining) and faster and easier implementation than EMP Mg mapping. As
172 colonies with known sampling date were selected, the absolute age of each growth ring could
173 be determined. [Figures 2a to 2c](#) show an example of correlation between growth ring, spatial
174 location, age and lead content in a sample collected in 2002 (Medes sample). The error on the
175 determination of the number of annual rings is estimated to be ± 10% relative.

176 *2.3 Analytical Methods*

177 *2.3.1 Electron microprobe and SEM mapping*

178 Electron microprobe chemical images of magnesium were obtained on thick polished samples
179 embedded in epoxy, on a SX100 CAMECA electron microprobe [Laboratoire Magmas et
180 Volcans (LMV), Clermont-Ferrand, France]. For image acquisition, the beam current, beam
181 diameter, counting times, and step interval varied in the range 10–50 nA, 1–2 mm, 30–50 ms

182 per pixel, 1–5 μm , respectively, with an acceleration voltage of 15 kV. All samples were
183 coated with an ~ 20 nm thick carbon layer.

184 All samples (including those studied by EMP) were examined with a field-emission
185 scanning electron microscope (FESEM) Raith Pioneer at CINaM (Marseille) in order to
186 image both growth rings and the ablation spots, and to correlate age and lead concentrations.
187 Images were obtained in BSE mode, with 20 kV accelerating voltage, 9.5 nA probe current,
188 and 6 mm working distance. To obtain clear images of entire analytical profiles, images at a
189 high spatial resolution were treated by Fourier transforms to enhance contrast (Perrin, 2014),
190 and assembled into large mosaics (see [Figure 2b](#) and [Figure 5a](#)).

191 2.3.2 Laser ablation ICP-MS

192 Most laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) analyses
193 were conducted at Laboratoire Magmas et Volcans in Clermont-Ferrand (France). Trace
194 element concentrations in calcite skeletons were obtained using an Agilent 7500-cs ICPMS
195 coupled to an Excimer Resonetics M-50 laser. The laser was operated at 193 nm wavelength
196 with 6–8 mJ energy, and 2–3 Hz pulse frequency. Spot size was 40 μm , with a spacing interval
197 of 100 μm in most analytical traverses. Ablation duration lasted about 100 s (blank count rates
198 were measured for 30 s prior to 70 s of ablation) in pure He atmosphere. The analyte was
199 carried to the ICP torch by a gas mixture wherein $\text{N}_2 + \text{Ar}$ were added to He. NIST 610 glass
200 standard was used for calibration (Gagnon et al., 2008). NIST 610 and BCR glasses were
201 analyzed every 15–20 spots as checks for precision. Duplicate analyses were obtained for
202 some coral samples to check for drift and to confirm the reproducibility of the results from
203 one session to another. Internal instrumental (1σ) errors and detection limits for lead are most
204 frequently both within the range 0.01–0.02 $\mu\text{g/g}$, and always below 0.04 $\mu\text{g/g}$. Data were
205 processed with the GLITTER software (Van Achterbergh et al., 2001).

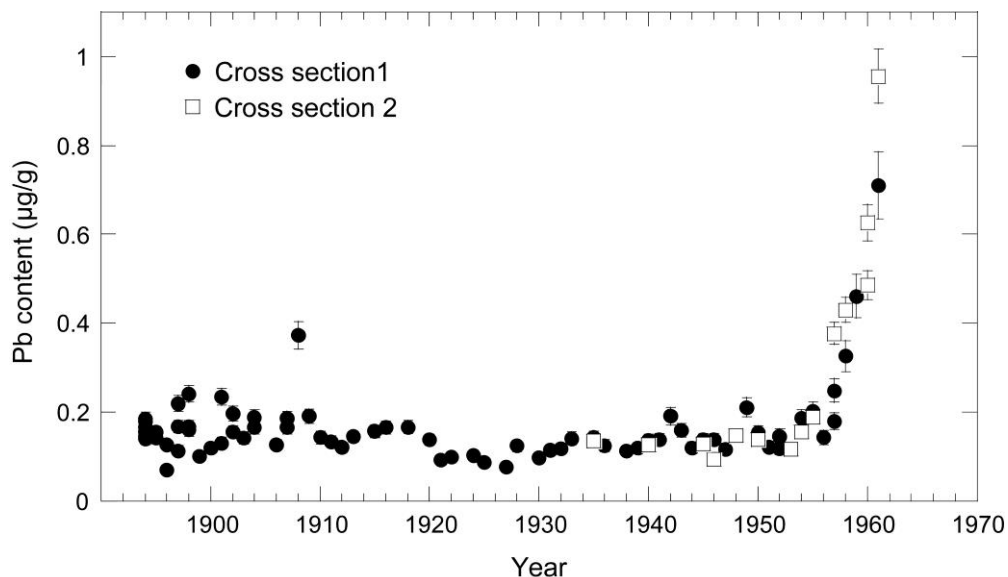
206 At Virginia Tech, minor and trace element abundances of coral samples were
207 determined by LA-ICPMS using an Agilent 7500ce quadrupole ICP-MS and a Lambda
208 Physik GeoLas 193 nm ArF excimer laser ablation system. The laser is coupled to an
209 Olympus petrographic microscope equipped with a 25× UV and visible Schwarzschild
210 objective (NA = 0.4) for analysis, plus 5× and 10× objectives for sample viewing. Four to six
211 spots were analyzed in each of 7 samples using a 60 μm spot size. He carrier gas flowed
212 through an ablation cell with a volume of ~1 cm³ at a flow rate of ~ 60 mL/min. Dwell times
213 were 10 ms for all elements and the oxide production rate was less than 1%. [Additional
214 information concerning the system is available at: <http://www.geochem.geos.vt.edu/fluids/>].
215 NIST 610 standard reference material (SRM) glass was analyzed two times before and after
216 each analytical session and was used as the external standard for data reduction and for drift
217 correction (Mutchler et al., 2008). Analyses of the NIST glass were accomplished using a
218 discharge voltage of the laser of 27 kV and a pulse rate of 15 Hz. The energy density at the
219 sample is a function of the aperture and attenuator settings which, for the analytical conditions
220 used here, results in an energy density on the sample of about 10±3 J/cm². Isotopes analyzed
221 included ⁷Li, ¹¹B, ²³Na, ²⁵Mg, ²⁷Al, ²⁸Si, ³⁹K, ⁴⁰Ca, ⁴⁹Ti, ⁵⁵Mn, ⁵⁶Fe, ⁶³Cu, ⁶⁶Zn, ⁷⁵As, ⁸⁸Sr, ⁸⁹Y,
222 ⁹⁰Zr, ⁹³Nb, ¹³⁸Ba, ¹³⁹La, ¹⁴⁰Ce, ¹⁴³Nd, ¹⁴⁷Sm, ¹⁵³Eu, ¹⁵⁷Gd, ¹⁶³Dy, ¹⁶⁶Er, ¹⁷²Yb, ²⁰⁸Pb, ²³²Th and
223 ²³⁸U. Calcium was used as an internal standard assuming a stoichiometric concentration of
224 calcium in the calcium carbonate. For each LA-ICPMS analysis, background signal was
225 collected for approximately 30-40 seconds before the laser shutter was opened to begin to
226 ablate the sample. The ablation was stopped after a few 10s of seconds and the signal was
227 collected until intensities returned to background levels. The initial few seconds of data from
228 each analysis was not included in data reduction to avoid possible errors from contamination
229 on the sample surface from airborne particles or previously ablated material deposited onto

230 the surface. Only the relatively stable, flat-topped portion of the ablation spectrum was used
231 to calculate element abundances.

232 3. Results

233 3.1 Lead contents and profiles in recent *C. rubrum* skeletons from the Mediterranean

234 The sample collected in 1962 near Cap de Creus (Spain) provides lead contents down to the
235 late nineteenth century period (~1894 AD). A first profile was obtained in the basal part of the
236 colony, providing a larger time span than a second profile collected in the upper part of the
237 colony. **Figure 3** shows the lead content as a function of time along two profiles.



238

239 **Figure 3:** Two Pb profiles obtained in a *C. rubrum* colony from Cap de Creus collected in
240 1962.

241

242 A good correlation is observed between the two profiles that display a flat signal with low Pb
243 levels between 1900 and 1955 followed by a sharp increase in the Pb content starting in 1955.

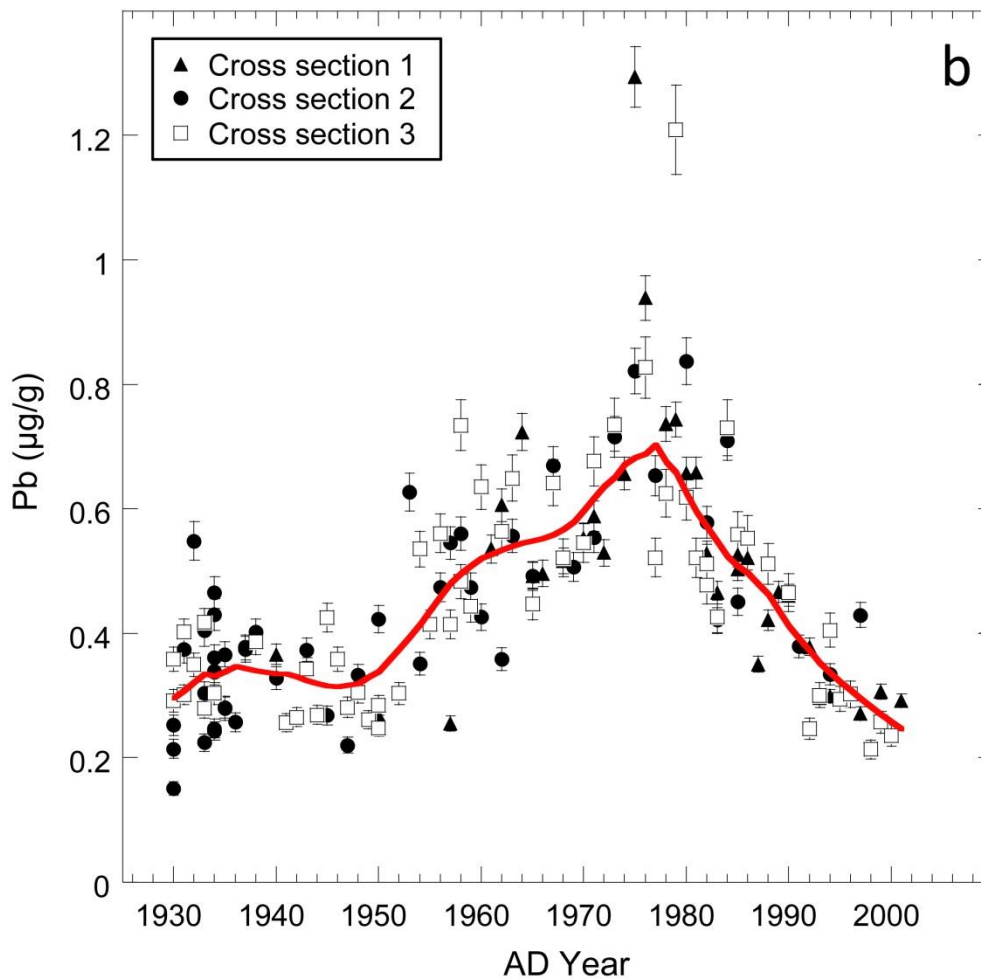
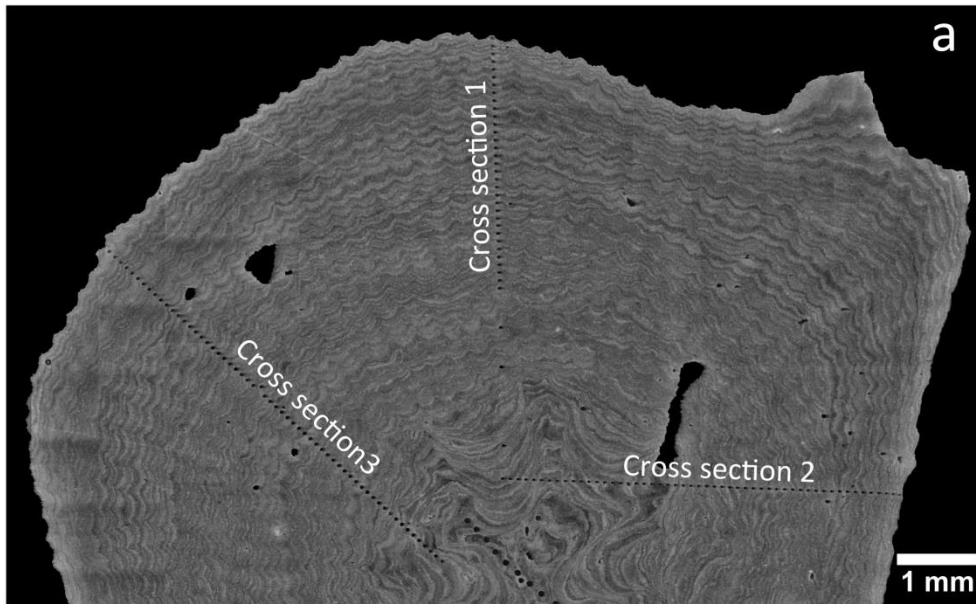
244 The very edges of the two profiles obtained near the skeleton surface indicate unusually high
245 lead contents (1.39 µg/g and 3.37 µg/g) with respect to those measured in other samples
246 described below for the same period. In the last growth layers, preliminary synchrotron
247 tomographies indicate the presence of a porous network, absent in the underlying layers. This

248 feature could generate abnormally high lead contents (by lead adsorption at the surface of the
249 pores) that are difficult to reconcile with inner values. In the data presented below, care was
250 taken to start or end compositional profiles a minimum of 150 or 200 μm away from the
251 skeleton surface. In the case of the Cap de Creus sample, the values obtained in the layer
252 closest to the skeleton surface were discarded and are not shown in **Fig. 3**.

253 The skeleton section in the Medes colony that was collected in 2002 is about 1 cm in
254 diameter and developed over the period 1930-2002. Three LA-ICPMS profiles were obtained
255 and SEM images were assembled to obtain a detailed map of the sample (**Figure 4a**). **Figure**
256 **4b** shows the 3 profiles, including profile 1 presented as an example in **Figure 2**. Data have
257 been fitted with a locally weighted least square error method. The data dispersion on both
258 sides of the fitting curve is relatively low ($\sim \pm 0.1 \mu\text{g/g}$), except at the maximum
259 concentrations where two values close of $1.2 \mu\text{g/g}$ depart from the fitted trend shown in red.
260 The three profiles show similar patterns. Starting in 1930, a relatively constant lead content of
261 about $0.3 \pm 0.1 \mu\text{g/g}$ is observed and continues to about 1952. After 1952, lead concentrations
262 increase rapidly at first (1952-1960), then more slowly (1960-1970), then increase rapidly
263 again (1970-1980) to reach a maximum of about $0.7 \mu\text{g/g}$ at the end of the 1970s. This sample
264 confirms that the increase of lead concentration began during the period 1952-1958 as is also
265 observed in the Cap de Creus sample. From 1980 to 2000, the lead contents in Medes 2002
266 decreases to reach values close to or slightly below those measured in 1930 (mean value
267 calculated within the interval 1998-2002: $0.26 \pm 0.01 \mu\text{g/g}$).

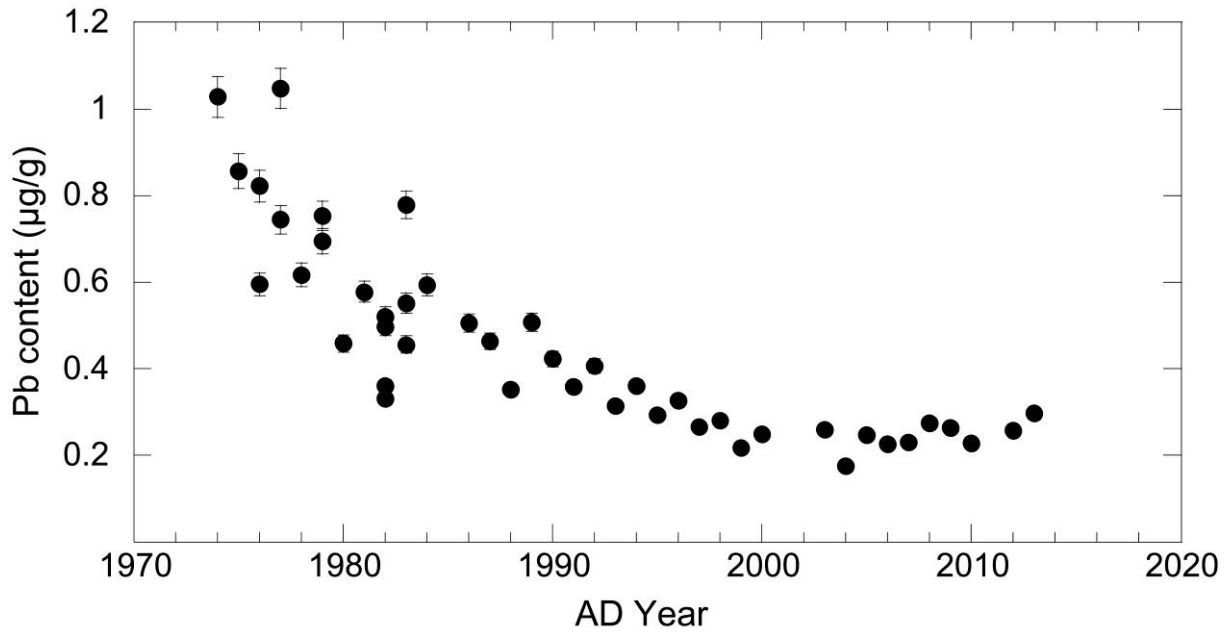
268 Another sample collected at the same location in 2014 (Medes 2014) provides
269 additional data for the period 1974-2014 (**Figure 5**). The data confirm the decrease of lead
270 content between 1980 and 2000 and indicates a stabilization of the lead concentrations at
271 about $0.25 \mu\text{g/g}$ for the period 1998-2014.

272



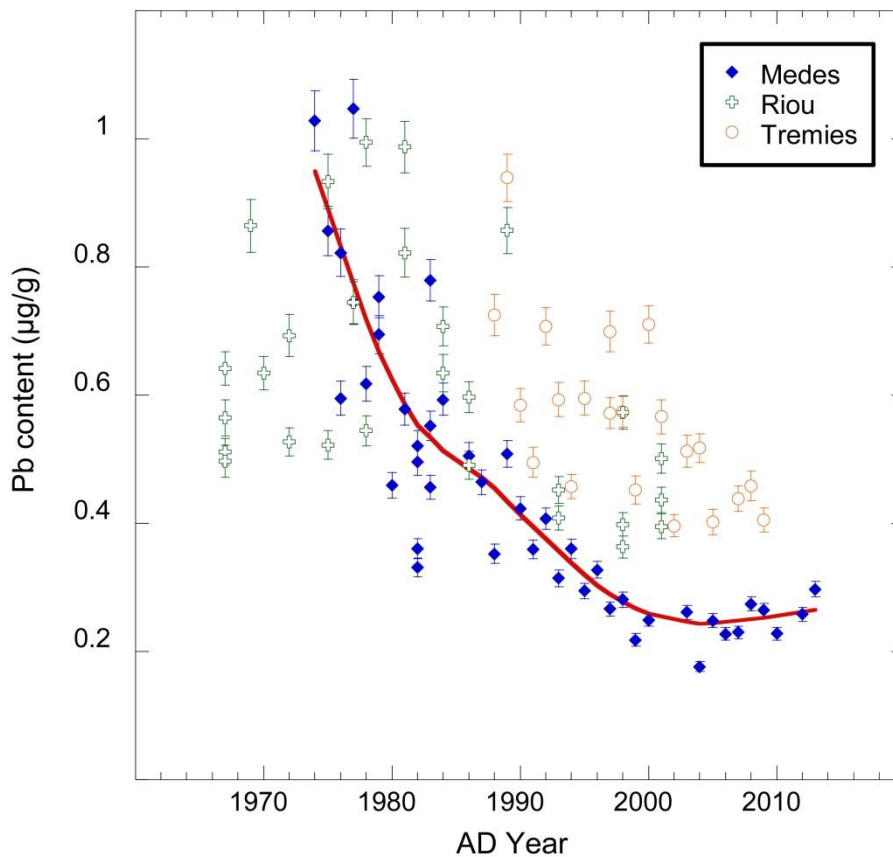
273

274 **Figure 4:** Lead profiles in *Medes* samples. a) Mosaic of SEM images of a coral collected in
 275 the *Medes* Islands in 2002. The black dots represent the spots of the LA-ICPMS analyses and
 276 mark the locations of the three profiles. b) Pb contents along the 3 profiles. Data have been
 277 fitted using a locally weighted least square error method (red curve).
 278



279

280 *Figure 5: Pb profile obtained in a sample collected at Medes in 2014*



281

282

283 **Figure 6:** Pb profiles in 3 different colonies recently collected near the Medes Islands, Riou
 284 Island, and Tremies cave in 2014, 2002 and 2010, respectively. Riou Island and Tremies cave
 285 are close to Marseille, a highly populated area. The Medes data have been fitted using a
 286 locally weighted least square error method.

287 The data obtained from three coral skeletons collected at different locations (Riou
288 2002, Medes 2014, Tremies 2010) are compared in **Figure 6**. Although the concentrations
289 differ, a decrease of Pb content with time is observed in all samples. After 1980, the red coral
290 from Medes 2014 shows lower Pb contents than the two others. The differences are
291 interpreted in terms of local effects related to geology, river inputs, or human activity
292 including lead mining and processing activities.

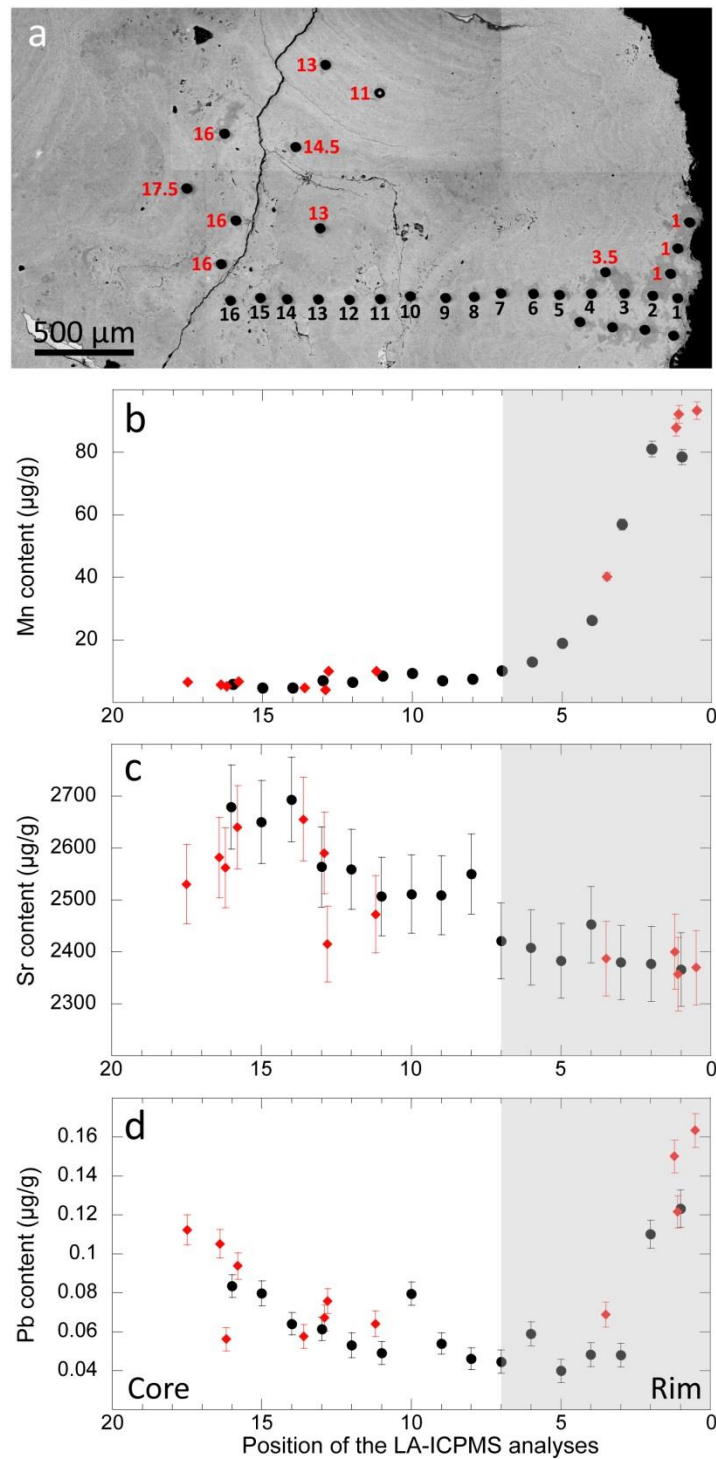
293 Data obtained on *C. rubrum* samples from Italy and Algeria collected after 2010 are
294 listed in **Table 2** as supplementary materials. The mean lead compositions vary between 0.11
295 and 0.43 $\mu\text{g/g}$. The significance of these variations will be discussed below.

296 To summarize, the lead concentrations in *C. rubrum* skeletons show systematic
297 variations with time. Constant concentrations of about 0.2-0.3 $\mu\text{g/g}$ are observed during the
298 period 1890-1954, followed by an increase during the period 1954-1978, to reach a maximum
299 at about 0.8 $\mu\text{g/g}$ in 1978 \pm 2 years, and then a progressive decrease to \sim 0.25 $\mu\text{g/g}$ in 2000.
300 The period 2000-present is marked by a relatively constant lead concentration of about 0.25
301 $\mu\text{g/g}$. Local anthropogenic and natural effects influence the concentrations of lead in present-
302 day skeletons.

303 *3.2 Lead contents in sub-fossil C. rubrum skeletons from the Mediterranean*

304 In order to study the anthropogenic impact on the environment, it is important to determine
305 the reference level of lead concentration in the red coral before the development of human
306 activities. This is a difficult task as lead pollution associated with human activities started
307 \sim 5,000 years ago (Settle and Patterson, 1980). The sample collected in the sedimentary layers
308 of the Tremies Cave is about 2,000 year old which means that this colony grew during the
309 Roman period. Since then, it was buried in sediments. While the inner part of the skeleton
310 kept its original red color, the outer part became dark as a consequence either of the

311 degradation of organic matter or the presence of manganese and iron oxide deposits
 312 commonly found in shallow and dark submarine caves (Alloué and Harmelin, 2001).



313

314 **Figure 7:** Two thousand year old sub-fossil sample. a) SEM image of the sample collected in
 315 the sediments of the Tremies Cave and location of the LA-ICPMS spots (black numbers for
 316 the spots along the profile and red for spots elsewhere). b), c) and d) Mn, U, and Pb
 317 concentrations along the lead profile.

318

319 The interior of the skeleton displays the same crystallographic organization as present-day
320 skeletons (as determined by Vielzeuf et al., 2010) when observed with optical microscope or
321 SEM (see Fig. 7a). X ray diffraction analysis of this skeleton shows no difference when
322 compared to present day corals. Some elements display gradients in concentration from rim to
323 core of the skeleton. Magnesium and strontium increase slightly (Figure 7c). The largest
324 difference is observed with manganese, which decreases from $\sim 80 \mu\text{g/g}$ to $\sim 7 \mu\text{g/g}$ towards
325 the center (Figure 7b). It should be noted that even in the core, the Mn concentrations are
326 larger than in the present-day *C. rubrum* skeletons (~ 7 compared to $\sim 1.5 \mu\text{g/g}$ – Vielzeuf et al
327 2018). To a lesser extent, uranium follows the same trend from core to rim but concentrations
328 in the core are similar to those observed in present-day *C. rubrum* ($\sim 0.08 \mu\text{g/g}$). These
329 observations, in particular the high concentrations of manganese, are attributed to diagenetic
330 mobilization of Mn from within the sediments (Brand and Veizer, 1980; Gillikin et al., 2005;
331 Kaufman et al., 1996). Concerning lead, the concentrations close to the rim ($\sim 0.14 \mu\text{g/g}$) are
332 higher than those in the interior of the skeleton. To determine a mean lead content of *C.*
333 *rubrum* in the pre-industrial period, analyses close to the edge were discarded (Figure 7d – the
334 grey area) and the value of $0.07 \pm 0.02 \mu\text{g/g}$ for Pb concentration is obtained.

335 The Sciacca corals provide another opportunity to determine a background level of
336 lead in the corals prior to extensive human activities. A sample of Sciacca coral was analyzed
337 at LMV; it showed lower concentrations in sodium, phosphorus, potassium, and higher
338 concentrations in manganese (41 ± 10 vs $1.4 \pm 0.3 \mu\text{g/g}$) and uranium (0.14 ± 0.02 vs $0.06 \pm$
339 $0.02 \mu\text{g/g}$) than present-day *C. rubrum* skeletons (supplementary materials, Table 2).
340 Concerning Mn, no concentration gradient was observed. Lead contents increased close to the
341 edge of the sample but reached a plateau inside the skeleton. Discarding some values at the

342 edge of the sample, a value of $0.09 \pm 0.01 \mu\text{g/g}$ was obtained for lead contents in these ancient
343 *C. rubrum* skeletons.

344 As stated above, another set of Sciacca and present-day *C. rubrum* skeletons were
345 analyzed at Virginia Tech (VT) (Supplementary materials – Table 3). The Sciacca samples
346 dated ~2100-2400 BP and ~4050-4400 BP represent times before the widespread introduction
347 of Pb into the environment through human activities. Interestingly, the mean concentrations
348 measured on present-day corals in this dataset are remarkably consistent with those
349 determined by Vielzeuf et al. (2018), except for K and Zn that show slight differences. In the
350 VT dataset, compared to present-day corals, the sub-fossil samples are enriched in Mn ($48 \pm$
351 17 vs $0.9 \pm 0.5 \mu\text{g/g}$), Fe (172 ± 107 vs $0.69 \pm 0.04 \mu\text{g/g}$), Cu (1.6 ± 1.6 vs $0.15 \pm 0.02 \mu\text{g/g}$),
352 and U (0.26 ± 0.15 vs $0.08 \pm 0.04 \mu\text{g/g}$). These high concentrations can be attributed to
353 diagenetic processes as will be discussed below. An important question is to determine
354 whether the lead contents are also affected by diagenetic transformations. In the Sciacca
355 compositions listed in Table 3 (supplementary materials), two groups can be distinguished on
356 the basis of Mn and Fe concentrations, with cutoff limits at 50 and 150 $\mu\text{g/g}$ for Mn and Fe,
357 respectively. The highest Fe and Mn concentrations are observed in the oldest samples (4050-
358 4400 BP). No change of lead concentration is observed between these two groups. Thus, the
359 impact of diagenesis on lead concentrations seems to be limited and a value of 0.10 ± 0.03 is
360 retained as the original content of lead in these corals.

361 Considering the three types of sub-fossil samples (Tremies cave 2000, Sciacca LMV,
362 Sciacca VT), a mean value of $0.09 \pm 0.03 \mu\text{g/g}$ will be taken as the lead concentration in sub-
363 fossil *C. rubrum* skeletons from the Mediterranean, keeping in mind that the lowest lead
364 contents measured are ca $0.04 \mu\text{g/g}$, and that natural local effects (geology hydrology, marine
365 currents) can also affect the original lead concentrations in these corals.

366 *3.3. Coralliidae from other oceans*

367 *Corallium rubrum* and other *Coralliidae* from the Atlantic Ocean

368 Previous comparative studies of *Corallium* species from the Mediterranean, Atlantic and
369 Pacific Oceans showed that the mineralogy, crystallographic structure, overall chemical
370 compositions, and skeleton growth modes are similar (Perrin et al., 2015). This similarity
371 justifies a comparison of their lead contents and allows covering a larger geographic area than
372 the Mediterranean alone.

373 Compositional profiles obtained on two samples of *C. rubrum* from the southern
374 coasts of Portugal collected in 2012 do not show compositional variations; their mean
375 concentrations is 0.22 ± 0.06 $\mu\text{g/g}$, close but slightly lower than the lowest values recorded in
376 the Medes 2014 sample for the period 1998-2014. The main difference between the Portugal
377 and Medes samples is that the first ones do not show lead content decrease in the profile,
378 meaning that the lead content had been almost constant in these corals for the last ~25 years.

379 Samples of *C. johnsoni* from the Azores islands collected in 2011 show no lead
380 concentration variations along two ~3000 and ~4000 μm long traverses. The mean lead
381 concentration in *C. johnsoni* is low: 0.10 ± 0.03 $\mu\text{g/g}$. The results obtained on *C. niobe* from
382 the same location in the Atlantic are remarkably similar, with a mean lead concentration of
383 0.11 ± 0.03 $\mu\text{g/g}$, along a 5500 μm diametral traverse.

384 *Coralliidae* from the Pacific Ocean

385 Pacific Ocean samples of *C. japonicum* and *C. konojoi* were analyzed from rim to core but no
386 SEM observation was carried out to identify and count the growth rings. Concerning the *C.*
387 *japonicum* sample collected in 2013, no variation was observed along a ~1800 μm long
388 traverse. However, with a mean of 0.16 ± 0.04 $\mu\text{g/g}$, lead concentrations are higher than in the
389 Azores corals from the Atlantic. Similar conclusions apply for a 2700 μm -long traverse in *C.*
390 *konojoi* collected in 2015, with a mean concentration of 0.17 ± 0.03 $\mu\text{g/g}$. Considering a
391 growth ring width of about $150 \mu\text{m year}^{-1}$, these traverses indicate that no significant change

392 of lead concentrations occurred during the last 10-20 years preceding their sampling in the
 393 Pacific. The mean Pb concentrations of all studied samples are given in **Table 1** (main text)
 394 and in **Tables 2 to 4** (supplementary materials). Lead contents along different profile are
 395 provided as supplementary materials in **Table 5**.

		Pb ($\mu\text{g/g}$) mean content	SD ($\mu\text{g/g}$)	n	Range of Pb concentrations	units
<i>C. rubrum</i>	Calcite					
Tremies 2000 year old		0.07	± 0.02	18	0.05 - 0.11	$\mu\text{g/g}$
Tremies 2010		0.61	± 0.15	27	0.40 - 0.94	$\mu\text{g/g}$
Cap de Creus 1962		0.17	± 0.09	75	0.07 - 0.71	$\mu\text{g/g}$
Medes 2002		0.46	± 0.18	146	0.15 - 1.29	$\mu\text{g/g}$
Profile 1		0.51	± 0.21	35	0.26 - 1.29	$\mu\text{g/g}$
Profile 2		0.42	± 0.16	52	0.15 - 0.84	$\mu\text{g/g}$
Profile 3		0.45	± 0.18	59	0.21 - 1.21	$\mu\text{g/g}$
Medes 2014		0.46	± 0.22	44	0.18 - 1.05	$\mu\text{g/g}$
Riou 2002		0.61	± 0.20	27	0.36 - 0.99	$\mu\text{g/g}$
Other Coralliidae (octocorals)	Calcite					
<i>C. niobe</i> 2005 (Azores)		0.12	± 0.05	14	0.06 - 0.28	$\mu\text{g/g}$
<i>C. johnsoni</i> 2011 (Azores)		0.11	± 0.04	25	0.06 - 0.23	$\mu\text{g/g}$
<i>C. japonicum</i> 2013 (Japan)		0.15	± 0.03	22	0.10 - 0.19	$\mu\text{g/g}$
<i>C. konojoi</i> 2015 (Japan)		0.16	± 0.03	25	0.12 - 0.21	$\mu\text{g/g}$
Litterature data						
Desenfant et al. (2006)		0.04	± 0.02	84	0.02-0.08	$\mu\text{g/g}$
Mona Island coral (<i>Montastraea faveolata</i>)	Aragonite				9 - 40	nmolPb/molCa
Sinclair et al. (2011)					~ 0 - 0.14	$\mu\text{g/g}$
Bamboo coral (<i>Keratoisis</i> sp.) from SE USA	Calcite					
Inoue et al. (2006)					~ 0.01 - 0.07	$\mu\text{g/g}$
Porites coral from Japan	Aragonite					
Kelly et al. (2009)					4 - 65	nmolPb/molCa
John Smiths Bay - <i>D. labyrinthiformis</i>	Aragonite					
North Rock - <i>D. strigosa</i>	Aragonite				6 - 31	nmolPb/molCa
North Rock - <i>D. labyrinthiformis</i>	Aragonite				30 - 80	nmolPb/molCa

396

397 **Table 1** - Lead content of some calcitic *Corallium* skeletons and other calcitic or aragonitic
 398 corals.
 399

400 Summary of the observations:

401 (1) Lead concentrations in *C. rubrum* skeletons from the Mediterranean are stable for the
 402 period 1894-1955 and are within the range 0.2-0.4 $\mu\text{g/g}$; concentrations increase up to
 403 about 1-1.2 $\mu\text{g/g}$ during the period 1960-1978, then decrease progressively to stabilize and
 404 reach values in the range 0.2-0.4 $\mu\text{g/g}$ in present-day corals.

405 (2) Sub-fossil Mediterranean *C. rubrum* are enriched in Mn, Fe, Cu and U, and depleted in Sr,
 406 Na and Mg, in comparison to present-day *C. rubrum*. Their lead concentrations are ~ 0.09
 407 ± 0.03 $\mu\text{g/g}$.

408 (3) Lead concentrations in the Pacific *C. japonicum* and *C. konojoi* are lower than in the
409 Mediterranean *C. rubrum*, with values close to $0.17 \pm 0.03 \mu\text{g/g}$.

410 (4) The lowest lead concentrations in present-day samples are found in two *Corallium* species
411 from the Azores islands in the Atlantic ($0.11 \pm 0.03 \mu\text{g/g}$).

412 4. Discussion

413 4.1 Lead in biogenic carbonates

414 The content of Pb in *Corallium rubrum* skeletons can be compared with other octocorals
415 (calcite skeleton) or hexacorals (aragonitic skeleton) (Table 1 and references therein). Sinclair
416 et al. (2011) reported a maximum Pb content of about $0.13 \mu\text{g/g}$ in the deep-water bamboo
417 octocoral *Keratoisis sp.*, at least 2 times lower than in the red coral. Lead contents in
418 scleractinian corals made of aragonite reported by Shen and Boyle (1988), Desenfant et al.
419 (2006) and Kelly et al. (2009) are within the range $0.01\text{-}0.2 \mu\text{g/g}$, *ca* an order of magnitude
420 lower than those recorded in *Corallium* skeletons made of high magnesium calcite. For
421 example, Desenfant et al. (2006) observed a peak in Pb content along a profile in Mona Island
422 hexacoral skeletons at about $0.08 \mu\text{g/g}$ whereas a peak is observed at $1\text{-}1.2 \mu\text{g/g}$ in the
423 Mediterranean *C. rubrum* for the same period. This is not necessarily an expected result
424 considering that the calcium cation site that may accommodate the larger Pb cation is larger
425 in aragonite than in calcite. Thus, the aragonite structure accommodates Pb substitution more
426 easily, which is consistent with the fact that PbCO_3 (cerussite) forms an isostructural solid
427 solution with aragonite. How can we explain this apparent inconsistency? The LA-ICPMS
428 analyses of lead in *Corallium* species presented here have been carried out in three different
429 laboratories (ETH-Zurich, Switzerland; Virginia-Tech, USA; and LMV Clermont-Ferrand,
430 France) on similar samples and the results are consistent. For this reason, an error greater than
431 50% relative for our measured lead concentrations is excluded. Also, the interpretation that Pb
432 cannot enter the calcite structure does not hold if the case of Sr, with an effective ionic radius

433 (IR) similar to the radius of Pb is considered [$IR_{Ca} = 1.0\text{\AA}$, $IR_{Pb} = 1.19\text{\AA}$, $IR_{Sr} = 1.18\text{\AA}$, in
434 sixfold coordination, (Shannon, 1976)]. Indeed, large amounts of Sr (*ca* 3000 $\mu\text{g/g}$) are
435 incorporated into *Corallium* high magnesian calcites (Hasegawa et al., 2010; Vielzeuf et al.,
436 2018; Vielzeuf et al., 2013; Weinbauer et al., 2000). Finally, it should be noted that *Corallium*
437 biogenic calcites are defective crystalline structures both from a structural (Perrin et al., 2015)
438 and chemical point of view. The incorporation of cations like Mg, Sr, Na and organic matrix
439 promotes the formation of defects in calcite, and this in turn, may allow calcite to
440 accommodate lead in its structure. The difference in lead concentrations in aragonitic and
441 calcitic *Corallium* species may not be a result of structural differences but, rather, may reflect
442 varying availability of lead in the seawaters in which the corals are growing. Another
443 possibility suggested by Rosenheim et al. (2005) to explain lead concentration differences
444 between sclerosponge aragonite and aragonite from zooxanthellate corals (10 times more Pb
445 in sclerosponges) is that pumping and filtering seawater and particulates is the only source of
446 nutrition for *Corallium* species, while zooxanthellate corals receive additional nutrients from
447 their algal symbionts. Nevertheless, except in the Mediterranean where the lead contents in *C.*
448 *rubrum* can be high and close to 1.2 $\mu\text{g/g}$, concentrations in *Corallium* from the Atlantic and
449 the Pacific are rather low and closer to the values measured in aragonitic corals in the above-
450 mentioned studies.

451 At this stage, it is worth mentioning that *Corallium* species incorporate significant
452 amounts of organic matrix (between 20,000 and 40,000 $\mu\text{g/g}$ (Allemand, 1993; Vielzeuf et al.,
453 2018). In scleractinian corals, it is generally agreed that lead is preferentially concentrated in
454 coral tissues relative to skeletons (Barakat et al., 2015; Esslemont, 2000; McConchie and
455 Harriott, 1992). To our knowledge, lead contents in octocorals tissues have not been studied
456 so far, but a similar tendency can be expected. Thus, some lead could be associated with the
457 organic matrix in *Corallium* skeletons. Though this hypothesis cannot be discarded, this is not

458 our preferred interpretation. Indeed, no difference in lead concentration is observed between
459 medullar and annular zones of *C. rubrum*, in spite of the fact that the medullar zone is 10 wt%
460 richer in organic matrix than the annular zone (Vielzeuf et al., 2018). In addition, a fossil *C.*
461 *rubrum* of upper Pliocene age (Giampileri, Province of Messina, Sicily), not included in the
462 present study because of intense chemical transformations with total loss of organic matrix
463 and ~75% loss of magnesium, shows lead concentrations of about $0.3 \pm 0.2 \mu\text{g/g}$
464 (supplementary materials – Table 2). These values cannot be taken as original lead contents in
465 these *C. rubrum* skeletons, ca 2 million year ago, but they show that lead can be present in
466 calcite that is devoid of organic matrix.

467 Following on earlier work on lead in aragonitic or calcitic corals (Esslemont, 2000;
468 Hanna and Muir, 1990; Shen and Boyle, 1987), three hypotheses can be considered for the
469 incorporation of Pb in *Corallium* skeletons: (1) adsorption on skeleton surfaces (or pore
470 surfaces), (2) lead binding by organics in the organic matrix, and (3) substitution of lead in the
471 calcite structure. The unusual high lead contents close to the surface of *Corallium* skeletons
472 (last growth rings) described above can be attributed to option (1) and data from the last
473 growth rings were discarded from lead traverses. Inside the skeleton, this hypothesis is
474 discarded due to the density of the inner skeleton. The hypothesis of organically bound lead
475 (2) cannot be discarded, but is difficult to verify and quantify. In our opinion and for reasons
476 given in a previous paragraph, the most plausible origin for the presence of lead in *Corallium*
477 skeletons is Pb cations substituting in the cation site (option 3).

478 4.2 Significance of lead concentrations and diagenetic indicators in sub-fossil corals

479 The quest to determine lead contents in *Corallium* skeletons that developed prior to recent
480 human impact led to the study of sub-fossil corals. As seen above, contents of Mg, Sr, and Na
481 are lower in sub-fossil corals than in present-day corals, while contents of Mn, Fe, Cu are
482 higher. These are expected features in carbonates that underwent early diagenetic

483 modifications (Brand and Veizer, 1980; Swart, 2015; Ullmann and Korte, 2015). The case of
484 elements with multiple oxidation states is interesting. As stressed by Ullmann and Korte
485 (2015) manganese and iron concentrations are low in oxygenated seawaters because they
486 precipitate as oxy-hydroxy phases (Crerar and Barnes, 1974; Glasby and Schulz, 1999). As a
487 consequence, Fe and Mn concentrations are low in biogenic calcites. Under reducing
488 conditions such as might occur in organic-rich sediments, the oxidation state of these
489 elements can change and Mn and Fe can enter the calcite structure (Brand and Veizer, 1980;
490 Thomson et al., 1986). Indeed, isostructural solid-solutions exist between calcite,
491 rhodochrosite (MnCO_3), and siderite (FeCO_3). The status of U in carbonates during diagenesis
492 is not so well documented. The difference between present-day and sub-fossil corals favors an
493 enrichment of U during diagenesis. Concerning lead, a main question that remains is whether
494 lead concentrations in *C. rubrum* are affected by diagenesis. **Figure 7** indicates that lead
495 concentrations increase at the edge of the coral skeleton. By analogy with Mn content, this
496 increase could be interpreted in terms of progressing diagenetic transformation. However, it
497 could also be interpreted as a rim effect as observed in present-day samples. The diagenetic
498 effect on the concentration of lead could thus be minimal, which is in agreement with the fact
499 that lead concentrations in the Sciacca corals are still low compared to present-day corals.

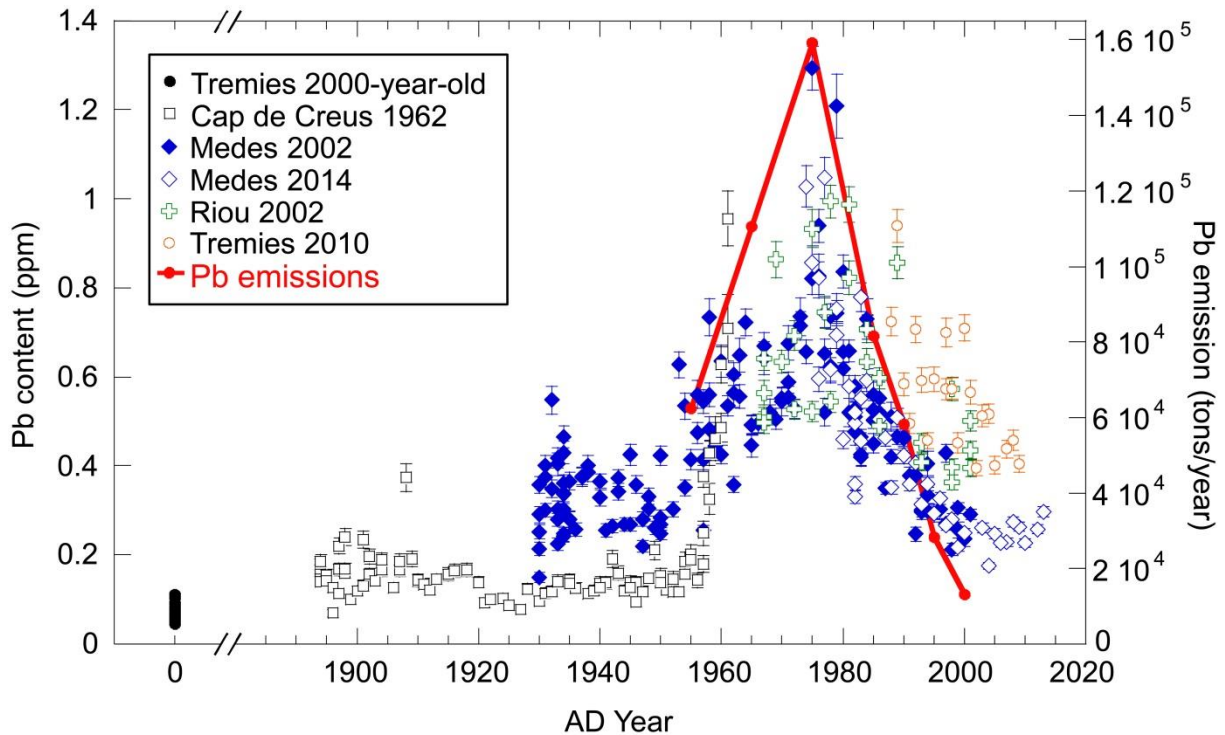
500 4.3 Interpretation of lead variations in *Corallium* skeletons

501 The present study answers the question of the origin of the large variation of lead content
502 observed in *C. rubrum* skeletons by Vielzeuf et al. (2018): lead contents depend on the date
503 and place of coral growth.

504 4.3.1 Temporal variations in lead content in *Corallium* skeletons

505 Five stages can be considered for the evolution of lead content in *C. rubrum* with time: (1) a
506 pre-industrial content in the two thousand years and older samples (**Fig. 7**), (2) a plateau for
507 the period 1895-1955, possibly with a slight decrease during the period 1905-1930 (**Figs 3 and**

508 8), (3) a sharp increase starting in 1955 and reaching a peak in 1974-1980, possibly with a
 509 shallower slope for the period 1962-1970 (Figs 4 and 8), (4) a sudden decrease tending toward
 510 a lower plateau during the period 1977-2000 (Figs 5, 6 and 8), and (5) lead contents close to
 511 pre-1955 values after 2000 (Figs 5 and 6).



512

513 **Figure 8:** Summary of Pb profiles obtained in this study. Pb emissions recorded in Europe
 514 from 1955 to 2000 are reported for comparison (Pacyna et al., 2007; Pacyna and Pacyna,
 515 2000).

516

517 It is important to note that the pre-industrial value determined above in red coral
 518 skeletons (in the range 0.04-0.1 $\mu\text{g/g}$) cannot be necessarily taken as pre-anthropogenic
 519 concentrations as different studies point out that lead contamination already existed 2,000
 520 years ago due to lead mining and production during the Roman Empire and earlier (Nriagu,
 521 1998; Shotyk et al., 1998). Indeed, the use of lead in human civilization appeared very early,
 522 *ca* 6400 B.C. (Wertime, 1973) and the first noticeable trace of human lead pollution dates
 523 back to the late Bronze Age (\sim 1200 B.C.) (Hong et al., 1994; Martinez-Cortizas et al., 1997;
 524 Shotyk et al., 1998). It should also be noted, however, that one of the Sciacca samples was

525 formed ~4050-4400 BP and pre-dates the earliest anthropogenic lead pollution, and this
526 sample contains ~0.1 $\mu\text{g/g}$ Pb. Since the pioneering work of Clair Patterson and his group at
527 Caltech, it is well established that the use of leaded gasoline for better functioning of car
528 engines that started in 1923 in the USA and soon thereafter throughout the world had a
529 noticeable impact on the environment at a global scale (Murozumi et al., 1969; Patterson,
530 1965). These observations initiated a change of regulation and the USA started reducing the
531 lead concentration in gasoline through the adoption of new policies during the mid-1970s (see
532 Nriagu (1990) for a review). In European countries, restrictions on the lead content in
533 gasoline were gradual and finalized by the EU-regulation in 1989 and the Aarhus Treaty
534 signed in 1998 (von Storch et al., 2003). The cycle of lead increase and decrease covering the
535 period 1955-2000 in red coral skeletons (Figure 8) is an illustration of a pollution crisis
536 referred to as the 'lead gasoline anomaly' below. The total Pb emissions in Europe during the
537 period covered by the coral record (Pacyna et al., 2007; Pacyna and Pacyna, 2000) is plotted
538 in Fig. 8 for a comparison. By averaging the lead contents in the red coral skeletons during the
539 period (1955-2000), i.e. when Pb emissions in Europe are available, a linear (Pearson) cross-
540 correlation coefficient between Pb content in the coral skeleton and Pb emissions in Europe of
541 0.87 is observed ($p = 0.01$). Thus, the variations in lead contents in coral samples are well
542 correlated with variations of lead atmospheric inputs from Europe (Figure 8). The lead
543 profiles in the red coral are also in agreement with reconstruction of anthropogenic lead
544 emissions in France where the flux suddenly increased in ~1950, decreased progressively
545 during the period 1970-1985, and rapidly after that, as shown by Ferrand et al. (1999) in their
546 Figure 8.

547 The lead pollution cycle, or parts of it, has been registered in different contexts. Ice
548 core profiles in central Greenland show an increase in lead content during the period ~1880-
549 1910, followed by a decrease for the period ~1910-1940, a new increase for the period 1930-

550 1970, and a decrease in the interval 1970-2000 (Boutron et al., 2004; McConnell et al., 2002).
551 In the red coral profiles, the slight decrease during the period 1905-1930 could match the
552 decrease observed in ice records. This trend is also recorded in reconstructed atmospheric
553 deposition in sediments from Spain (Corella et al., 2017). In Greenland ice records, the lead
554 gasoline anomaly starts earlier than in the red coral (1935 vs 1955). This difference could
555 reflect a better sensitivity of ice than corals to record lead pollution. The pollution peak during
556 the lead gasoline anomaly is also slightly different (1970 in ice cores vs 1974-1980 in the red
557 coral). This could be attributed to earlier application of lead regulation in the US than in
558 countries around the Mediterranean. It will be noted that this decrease is in good agreement
559 with the decrease in lead concentrations observed in leaves and human blood for the same
560 period (von Storch et al., 2003). Finally, the return to a level prior to the use of leaded
561 gasoline is well marked in the red coral (Figs 5 and 6). This pattern is consistent with the
562 return of lead emissions in Europe to pre-1950 levels in the years 2000 (Miralles et al., 2006;
563 von Storch et al., 2003).

564 Studies on Pb contents in scleractinian coral skeletons also show lead variations during
565 the last decades in western North Atlantic areas (Kelly et al., 2009; Shen and Boyle, 1987) as
566 well as in the western Pacific Ocean (Inoue et al., 2006), Caribbean Sea (Desenfant et al.,
567 2006) and Indian Ocean (Lee et al., 2014). Records of lead pollution in other marine
568 organisms, such as Bamboo corals (Sinclair et al., 2011), sclerosponges (Lazareth et al., 2000)
569 and clams (Gillikin et al., 2005) are also available (see Shotyk and Le Roux (2005) for a
570 review). Figure 9 shows a comparison of Pb concentrations of the calcitic red coral skeletons
571 and three other aragonitic coral skeletons (Desenfant et al., 2006; Kelly et al., 2009) during
572 the last century. Even if Pb concentrations are different in the different corals, identical trends
573 are generally observed. However, it has been shown that the timing of the event can vary

574 significantly from one place to another, especially in the Indian Ocean (Lee et al., 2014),
575 probably due to differences in the timing of application of new regulations.

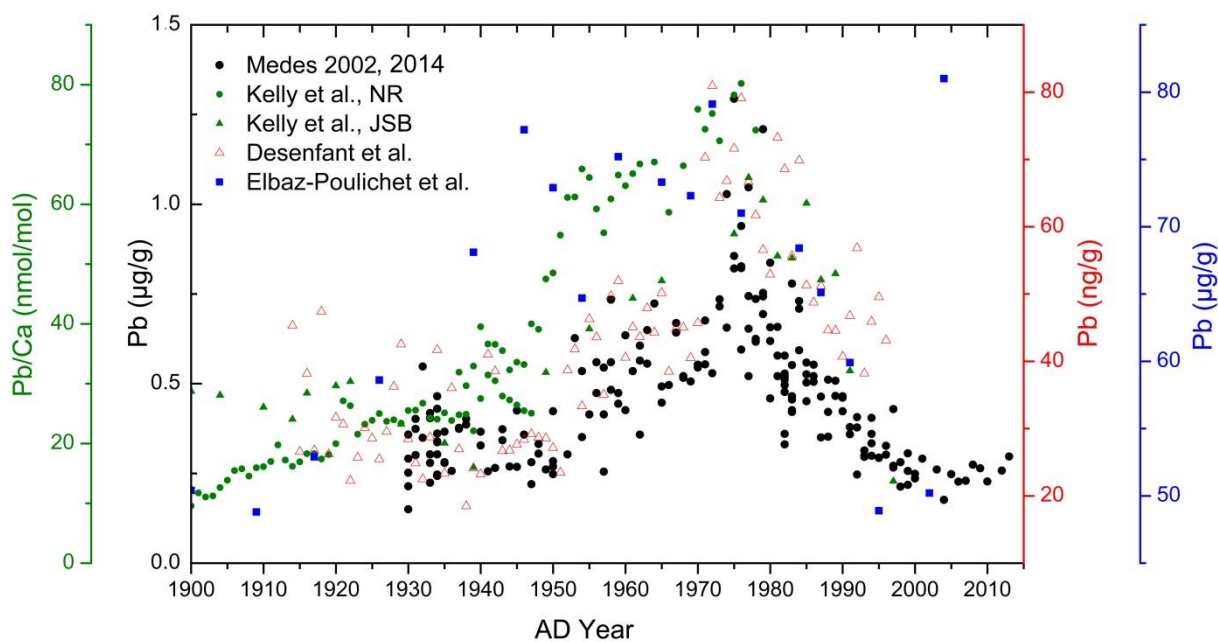
576 4.3.2 Spatial variations in lead content in *Corallium* skeletons

577 As discussed above, lead contents in precious *Corallium* species from the Mediterranean, the
578 Atlantic and the Pacific differ, probably indicating different levels of lead in the seawaters.
579 The Atlantic *C. rubrum* contains less lead than its Mediterranean analogue [mean value of
580 0.23 +/- 0.06 compared to 0.48 +/- 0.19 µg/g (Vielzeuf et al., 2018)] and does not show a
581 significant decrease for the period 1992-2012. We ascribe this difference to lead content
582 differences between the Atlantic Ocean and the Mediterranean Sea, as will be discussed
583 further below. More locally, the comparison of *C. rubrum* samples from different locations in
584 the Mediterranean for the period 1980-2010 (Figs. 6 and 8) indicates that the trends of
585 decreasing lead contents are identical but that the absolute values differ: the Medes 2014
586 sample displays the lowest contents, while Riou 2002 and Tremies 2010 (sampling sites
587 separated only by about ten kilometers) have similar contents. Differences can be explained
588 by the presence of ancient lead processing factories in the Marseille area (Daumalin and
589 Raveux, 2016) which locally contaminate the seawater (Laffont-Schwob et al., 2016). These
590 observations indicate that the red coral is sensitive to the overall pollution but also records
591 local effects. In particular places, red coral could be used to monitor the evolution in time of
592 specific anthropogenic lead pollutions. Here again, the situation is similar in scleractinian
593 coral, as Medina-Elizalde et al. (2002) showed differences of lead contents in the skeleton of
594 *Orbicella annularis* (formerly named *Monstastraea annularis*) from two distinct areas,
595 Cancún and Majahual, located about 300 km from each other. The Cancún area showed a
596 more important lead pollution due to its rapid human development.

597

598 4.4 Comparison with other lead records in the Mediterranean

599 In the western Mediterranean region, data acquisition of seawater and atmosphere Pb contents
600 started in the early 1980s and showed a decrease of Pb atmospheric concentration at the end
601 of the 1980s, delayed with respect to North America (Annibaldi et al. (2009); Migon et al.
602 (2008) and reference therein). This delay can be attributed to differences in the timing of
603 implementation of lead gasoline regulations between Europe and the USA.



604
605 **Figure 9:** Pb concentration profiles obtained in Medes 2002 and 2014 (black dots) compared
606 with other records (green dots and triangles: two scleractinian corals from the Atlantic
607 Ocean (Kelly et al., 2009); red triangles: massive coral from the Caribbean Sea (Desenfant et
608 al., 2006); blue squares: sediment core from the Northwestern Mediterranean Sea (Elbaz-
609 Poulichet et al., 2011). The color of the Y-axis match the different datasets.
610

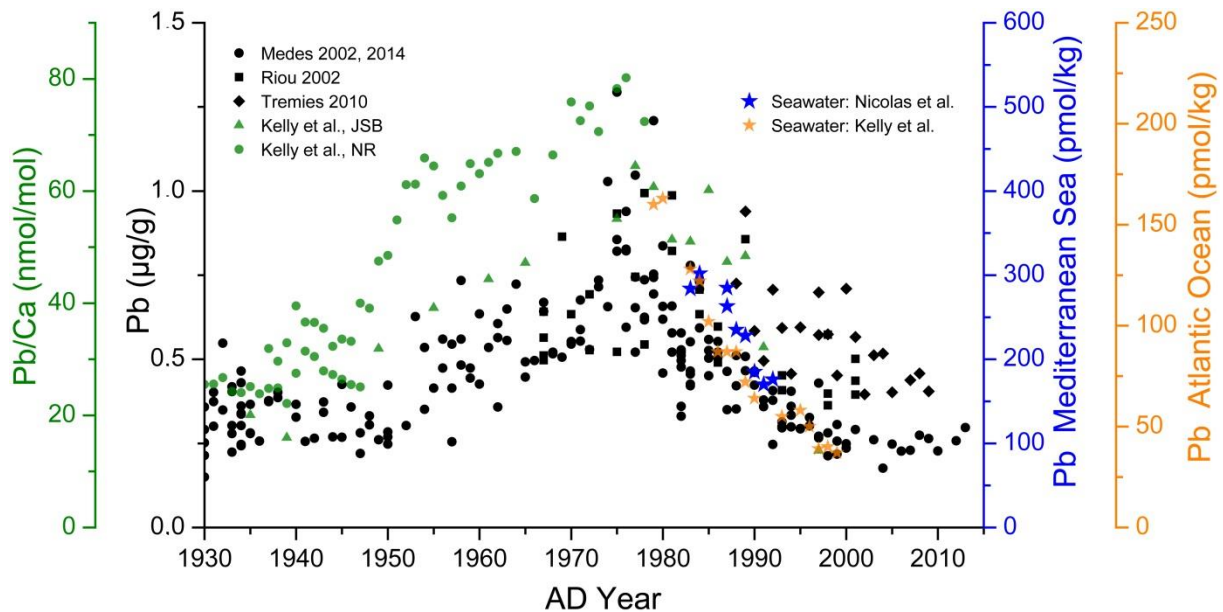
611 Although the measurement of Pb concentration in seawater and atmosphere is an effective
612 method to evaluate inputs of anthropogenic Pb, temporal records of Pb concentration are
613 limited. The current status of specific regional pollutions by metallic contaminants in the
614 Mediterranean basin has been the subject of studies using sea plants, mussels, seawater or
615 sediments (e.g., (Gosselin et al., 2006; Mikac et al., 2015; Serrano et al., 2011; Tranchina et
616 al., 2005). Mussels and sea plants are indicators of present-day local pollution in the
617 Mediterranean basin (Casas et al., 2008; Gosselin et al., 2006). However, such organisms do

618 not record lead variation over long periods of time, even if a correlation between lead
619 concentrations in a sea plant (*Posidonia oceanica*) and estimated lead emissions in the same
620 area is observed (Tranchina et al., 2005). Some studies provide lead profiles in Mediterranean
621 sediment cores (Elbaz-Poulichet et al., 2011; Miralles et al., 2006). The Pb concentrations
622 determined by Elbaz-Poulichet et al. (2011) are plotted in **Figure 9**. Corals and sediments
623 display similar trends but the sediment peak is wider. This difference can be explained by
624 possible disturbances associated with remobilization and bioturbation processes. Thus,
625 sediment cores provide information on lead contents covering several centuries. Nevertheless,
626 their temporal resolution is not as good as the annual resolution obtained with corals.

627 4.5 Lead contents in seawater

628 Data compiled by Annibaldi et al. (2009) give indications of relative lead contents in the
629 Pacific, Atlantic and Mediterranean; lead contents are lower in Pacific and Atlantic seawaters
630 than in the Mediterranean (0.05 ± 0.03 , 0.07 ± 0.06 , and 0.19 ± 0.11 nmol/L, respectively; means
631 of values tabulated in Annibaldi et al. (2009) – Table 5). A decrease of lead content in surface
632 seawaters in the western North Atlantic Ocean starting in the mid-1980s has been observed
633 and correlated to the leaded gasoline phase out in the USA (Wu and Boyle, 1997). **Figure 10**
634 shows Pb concentrations in Mediterranean and Atlantic seawaters (Kelly et al., 2009; Nicolas
635 et al., 1994), together with lead contents in aragonitic corals *Diploria labyrinthiformis* and *D.*
636 *strigosa* from Kelly et al. (2009), and calcitic *C. rubrum* from the present study. Using Pb
637 concentrations in aragonitic corals and seawaters, Kelly et al. (2009) determined an empirical
638 Pb partition coefficient between aragonite and seawater, defined as $Kd = [Pb/Ca]_{\text{aragonite}} /$
639 $[Pb/Ca]_{\text{seawater}}$, ranging from 2.8 to 3.6. These values allowed the authors to infer seawater Pb
640 concentrations before 1979. In the case of *Corallium* species, a new partition coefficient can
641 be proposed. As commonly assumed in this type of calculation (Kelly et al., 2009; Rosenheim
642 et al., 2005), a constant concentration of calcium in seawater ($[Ca]_{\text{seawater}}$) of 10.3 mmol/kg

643 from Bruland (1983) can be used. On another hand, Nicolas et al. (1994) determined Pb
 644 concentrations in the Northwestern Mediterranean seawaters ($[Pb]_{\text{seawater}}$) for the period 1983
 645 to 1992 ranging from 284 to 176 pmol/kg for the surface layer (10-100 m).



646
 647 **Figure 10:** Comparison between Pb concentrations in recent red coral skeletons (this study)
 648 and Pb concentrations of Mediterranean seawater (blue stars: (Nicolas et al., 1994), and Pb
 649 concentrations in two scleractinian corals and in Atlantic seawater (Kelly et al., 2009). Pb
 650 concentrations in corals are on the left Y-axis and Pb concentrations in waters are on the
 651 right Y-axis
 652

653 Using $[Pb]_{\text{calcite}}$ and $[Ca]_{\text{calcite}}$ of 0.48 and 350,000 $\mu\text{g/g}$, respectively (Vielzeuf et al., 2018),
 654 the calculated partition coefficient varies from 10 to 16. To avoid the uncertainty associated
 655 with a calcium content in seawater that depends on salinity, a simpler ratio can be used
 656 instead to calculate the lead partitioning: $D = [Pb]_{\text{calcite}}/[Pb]_{\text{seawater}}$ (concentrations expressed
 657 in pmol/kg). Considering lead contents in *C. rubrum* of 0.63 $\mu\text{g/g}$ in 1983, and 0.45 $\mu\text{g/g}$ in
 658 1992 (Fig. 8), D_{1983} and D_{1992} equal 10,706 and 12,340, respectively. A mean D of $\sim 11,500$
 659 will be considered as our best estimate. Concerning the *Corallium* species from the Atlantic
 660 (Azores Islands), using the lead content in Atlantic seawaters given by Kelly et al. (2009)
 661 (Fig. 10) and lead concentrations of 0.11 $\mu\text{g/g}$ determined above, K_d and D are equal to 12.5
 662 and 10,617, respectively, in agreement with partition coefficients determined in the

663 Mediterranean. These partition coefficients allow us to calculate an approximate Pb
664 concentration of 400 pmol/kg in the seawater of the northwestern Mediterranean during the
665 mid-1970s. The highest values could have reached around 550 pmol/kg at the maximum of
666 the pollution crisis. **Table 5** (in supplementary materials) lists some lead contents in present-
667 day *C. rubrum* skeletons, collected in various places in the Western Mediterranean, and in
668 rings that formed after the year 2000. This table shows that lead concentrations still vary
669 depending on location in the Mediterranean. The lowest value at 0.11 µg/g, close to pre-
670 industrial contents, comes from the Montecristo Island, an Italian Natural Reserve since 1971,
671 and one of the least accessible and most protected areas in the Mediterranean Sea (Turicchia
672 et al., 2018). At the opposite, the highest values (Alghero, Sardinia; Marseille area) come
673 from places where lead was historically extracted or processed. Nevertheless, values
674 comprised between ~50 and ~200 pmol/kg remain below the standard values adopted in Italy
675 to guarantee (1) human health over short periods of time, or (2) the defense of the aquatic
676 ecosystem on long terms [720 and 290 pmol/L, respectively - Annibaldi et al. (2011)]. The
677 estimated values of present-day seawater lead contents (**Table 5** – supplementary materials)
678 are in good agreement with data from the central Adriatic Sea in 2004 of 130 pmol/L
679 (Annibaldi et al., 2009) and data from the outer Saronikos Gulf, Greece, of 128 pmol/L
680 (median value between 2000 and 2010) (Paraskevopoulou et al., 2014). Nevertheless, some
681 specific areas in the Mediterranean Sea still have high Pb concentrations, such as the Ancona
682 coast of the Central Adriatic Sea [560 pmol/L, (Annibaldi et al., 2011)], or the inner
683 Saronikos Gulf [2600 pmol/L, (Paraskevopoulou et al., 2014)].

684 5. Conclusion

685 Various environmental, structural and chemical factors make the red coral and other calcitic
686 *Corallium* species good recorders of lead pollution in the Mediterranean and other oceans.
687 *Corallium* skeletons grow slowly, producing records over long periods of time in a single

688 colony. The annual character of growth rings is well-established, and rings can be easily
689 identified by non-destructive methods (SEM), allowing the precise positioning (space and
690 age) of *in situ* chemical analyses, and possibly, multiple analyses of a single ring. *C. rubrum*
691 grows at different depths (from the surface to great depths ~1,000 m) allowing the study of
692 large domains in the sea. Precious corals have been used in jewelry since the Neolithic
693 (Skeates, 1993) and ancient corals can be recovered, dated and analyzed in jewels and
694 sediments of different ages. Lead concentrations are high enough to be determined by *in situ*
695 high precision non-destructive methods (LA-ICPMS). Contrary to sediments or ice cores, a
696 partition coefficient of lead between biogenic calcite and seawater can be determined, which
697 allows the seawater lead content during the skeleton growth to be estimated. *Corallium*
698 skeletons can record both local and global effects, and the comparison of skeletons from
699 places with different levels of pollution allows one to separate local effects from global
700 effects. The response of the skeletons to emissions of lead in the environment is fast, probably
701 due to the fact that Pb has a residence time of about 2 years in ocean surface waters (Nozaki et
702 al., 1976).

703 The studied samples cover the entire cycle of the global lead gasoline pollution event,
704 from the beginning of the impact (in the 1950s) associated with the dramatic increase in the
705 number of cars in the world, to the application of new regulations starting in 1975, and a
706 return to pre-1950 levels in 2000. Twenty-five years of pollution were sufficient to produce
707 Pb levels in seawater that approached values known to endanger human health within short
708 periods of time and certainly endangering the aquatic ecosystem over longer periods of time.
709 A duration similar to that required to reach the pollution peak was required to return to the
710 pre-lead gasoline values. Lead mining and processing sites sustain lead pollution of seawaters
711 over longer periods of time, which emphasizes the need to remediate the industrial sites after
712 the cessation of their activities.

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