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ABSTRACT: Concentrations of Ba and Pb measured by LA-ICP-MS make it possible to distinguish the precious corals *Corallium rubrum* from the Mediterranean Sea and *C. japonicum* from the Pacific Ocean with a high degree of confidence. Compared to *C. japonicum*, *C. rubrum* coral contains higher Ba and Pb (>6 and >0.2 ppm, respectively). This chemical fingerprinting technique was developed by the authors' group during prior research and is successfully tested here on three polished red coral cabochons of known origin. This minimally destructive, relatively inexpensive and easy-to-implement method can help enforce trade regulations by distinguishing CITES-listed *C. japonicum* from non-CITES-listed *C. rubrum* precious corals.

Precious red coral, *Corallium rubrum* (originally Madrepora rubra, Linnaeus 1758; Figure 1), comes from the Mediterranean Sea and adjacent Atlantic Ocean (Zibrowius et al. 1984). It has been appreciated for its beauty and used in jewellery and objets d'art since antiquity (Hickson 1924; Tsounis et al. 2010; Iwasaki 2010; Cooper et al. 2011; Santangelo et al. 2012; Fürst et al. 2016). Mediterranean red coral has been supplied to the jewellery industry through two sources: primarily by fishing present-day colonies, and secondarily from stockpiles of long-dead coral branches collected from sea-floor sediments (mostly during 1875–1914; Bavestrello et al. 2021). Indeed, large amounts of C. rubrum red coral harvested in Italy in the last 150 years came from the sediments of the Sciacca banks of Sicily, Italy (Rajola 2012; Cattaneo-Vietti et al. 2016; e.g. Figure 2). For example, 16,330 t of Sciacca coral were collected over 34 years in the Sicily Channel from the late 19th to early 20th centuries (Cattaneo- Vietti et al. 2016). Jewels and beads of Sciacca coral are still commercialised, particularly from dealers in Torre del Greco, Italy, and in antiques markets. Other Corallium species, such as C. japonicum (Kishinouye 1903) and Pleurocorallium elatius (formerly C. elatius, Ridley 1882), both of which come from the western Pacific Ocean, have been traded since the second half of the 19th century (Cooper et al. 2011; Nonaka et al. 2014). Interestingly, long-dead coral branches (some exceeding 5,000 years old) have also been collected and traded in the Pacific since the 1900s (Okumura et al. 2021).

Various studies of precious corals concerning their history, economy, fishing techniques, biology, ecology, mineralogy, chemistry and crystallography are referenced in two proceedings of international workshops (Bussoletti et al. 2010; Precious Coral Protection and Development Association 2012). As noted by Cooper et al. (2011), precious corals are vulnerable to over-exploitation, and various trade regulations are enforced by different countries. International agreements concerning these species are promulgated by the Convention on International Trade

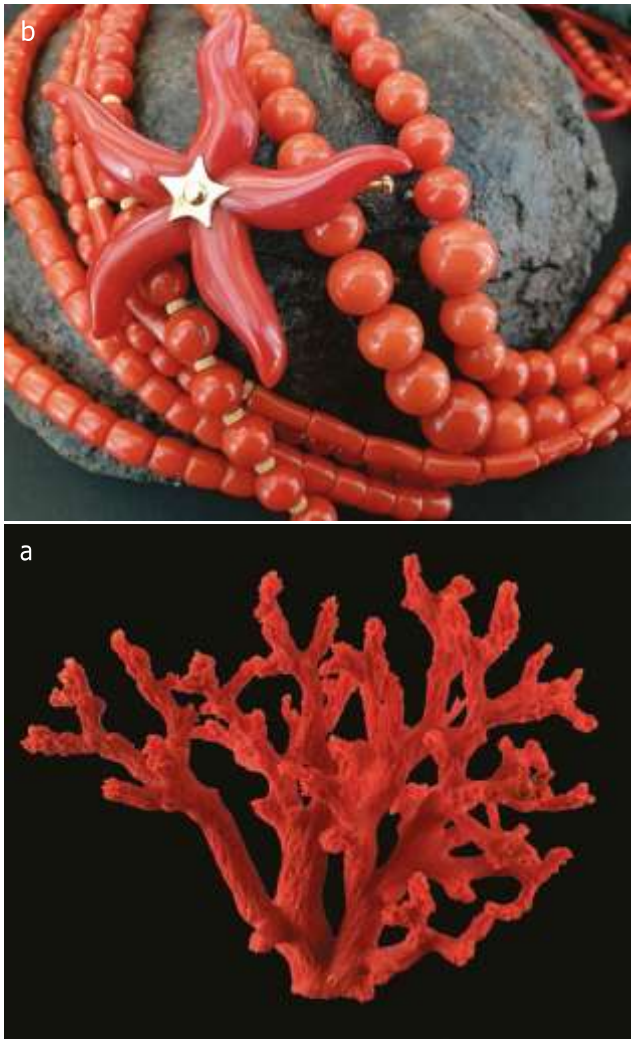

Figure 1: Precious coral is represented here by (a) a colony of Mediterranean red coral (C. rubrum) after removal of the organic tissues (80 g; basal diameter 21 mm), and (b) necklaces and a brooch of C. rubrum (beads 12 mm in maximum diameter and brooch 5 cm across). (a) Specimen provided by J. G. Harmelin and photo by D. Vielzeuf; (b) jewellery courtesy of C. Balme-Heuze, and photo by D. Vielzeuf and C. Balme-Heuze.

in Endangered Species of Wild Fauna and Flora (CITES). In 2011, four Coralliidae species (C. japonicum, Pleurocorallium elatius, P. konojoi and P. secundum[1], all from the Pacific Ocean) were listed in CITES Appendix III [2] (Table I). However, C. rubrum is not listed in CITES appendices and may be freely traded. Parties to the Convention are required to enforce CITES regulations for listed species, including control of documentation that accompanies exports and imports from registered companies. This enforcement may require the identification of the products on site. From the trade

perspective, this problem is covered in The Coral Book (CIBJO 2020). However, unambiguous identification criteria for polished coral products are scarce, debatable or difficult to implement.

Figure 2: Sciacca coral comes from sediments in the Sicily Channel, where catastrophic events in this tectonically and volcanically active area deposited broken branches of C. rubrum. This specimen (15.7 × 10.0 cm) consists of a mixture of Sciacca coral (orange), sediments (light brown) and calcareous worm tubes (white). Photo by G. Rajola.

Previous Work and Aims of the Present Study[1]

In two previous studies by the authors' group, more than 1,000 analyses were performed by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) on 36 different samples of C. rubrum, C. japonicum, P. elatius and P. konojoi (Vielzeuf et al. 2018; Ricolleau et al. 2019). The 2019 article focused on the variation of Pb contents in C. rubrum over several decades. The 2018 article examined variations in the concentrations of Ca, Mg, Na, Sr, S, Li, Ba, Pb and U—within a species and among different species—together with correlations between elements. We observed that some element concentrations (Ca, Mg, Na, Sr, Li and U) depend on growth rate, while others (Ba and Pb) do not. An important conclusion of this work was that the presence of growth rings (marked

1 The taxonomy used in this article follows the updated classification from the World Register of Marine Species (www.marinespecies. org/aphia.php?p=taxdetails&id=125325). However, renaming of taxa occurred in 2016, after the last CITES listings of precious corals, so CITES uses different biological names (e.g. C. elatius instead of P. elatius; see Table I). Note also that in jewellery industry terminology, 'precious coral' refers only to corals in the Coralliidae family, whereas in biological lexicon, 'precious coral' encompasses all corals that might be used for decorations.

2 CITES Appendix III is meant for species that are not endangered, but have been included at the request of a specific country that already has internal trade regulations in place and is seeking cooperation from other countries to help prevent what it considers to be unsustainable or illegal exploitation. For Coralliidae species currently listed in CITES Appendices, see https://tinyurl.com/h9seerz6.

Table I: Descriptions and definition of the precious corals in this study.[a]

Region	Current Scientific Name	CITES classifi-cation name	Commercial names	Colours	Fishing areas and depths	Morphology, size and weight	CITES Appendix	Notes and comments
Mediterra-nean Sea	*Corallium rubrum*[b]	*Corallium rubrum*	Mediterranean, Sardinian, Sardegna	Dark red, uniform red to dark orange	Primary: Western Medi-terranean Sea Secondary: Eastern Atlantic coast (south Portugal and north-west Africa) Depth: 50–1,000 m	Fan or bush shaped Avg. height: 10–20 cm Avg. trunk diam.: 8 mm Avg. weight: 50–300 g	Not included in any appendix	Can be exported and imported in every country
	Corallium rubrum	*Corallium rubrum*	Sciacca	Orange, pink and darkened 'smoked' orange	Long-dead *C.rubrum* recovered in Mediterranean Sea sediments, southern Sicily Depth: 30–60 m	Small broken branches Avg. height: 7–10 cm Avg. trunk diam.: 5 mm Avg. weight: 8–30 g	Not included in any appendix	Can be exported and imported in every country
Pacific Ocean	*Corallium japonicum*	*Corallium japonicum*	Aka, Moro, Oxblood	Dark red and very dark red with lengthwise white 'soul'	Japan Depth: 80–300 m	Fan shaped Avg. height: 5–30 cm Avg. trunk diam.: 5–25 mm Avg. weight: 100–500 g	Appendix III	CITES listing requested by China
	Pleuro-corallium elatius	*Corallium elatius* (red to dark pink)	Cerasuolo, Momo, Satsuma	Bright red, 'salmon', orange, dark pink and 'fl colour with lengthwise white 'soul'	Taiwan and Japan Depth: 150–350 m	Fan shaped Avg. height: 15–40 cm Avg. trunk diam.: 10–50 mm Avg. weight: 100–5,000 g	Appendix III	CITES listing requested by China
	Pleuro-corallium elatius	*Corallium elatius* ('fl pink)	Angel Skin, Boké, Magai, Peau d'Ange, Pelle d'Angelo	'Flesh' pink with different colour intensities	Japan and Taiwan Depth: 150–350 m	Fan shaped Avg. height: 15–40 cm Avg. trunk diam.: 10–50 mm Avg. weight: 100–5,000 g	Appendix III	CITES listing requested by China
	Pleuro-corallium konojoi	*Corallium konjoi*	Pure White, Shiro, Bianco	Milky white and red or pink, speckled white	South China Sea and Vietnam Depth: 80–300 m	Fan shaped Avg. height: 10–40 cm Avg. trunk diam.: 10–30 mm Avg. weight: 100–700 g	Appendix III	CITES listing requested by China

a Modified after CIBJO (2020). b The name 'corallium rubrum' (corallo rosso, corail rouge, coral rojo, etc.) has been used in Mediterranean cultures at least since the Renaissance, long before the attribution of a scientific name to this species (e.g. Mesue 1544). Thus, in Mediterranean cultures the name 'red coral' refers primarily to C. rubrum.

by variations in composition) in coral skeletons is due to the alternation of fast and slow growth stages during the year. Although differences in the concentrations of Ba and Pb between precious corals from the Mediterranean Sea and the Pacific Ocean were briefly mentioned in that work, we had not developed this point previously. The main goal of the present study was to determine whether precious corals have different chemical signatures that can be applied to their separation in a gemmological context. We performed a statistical analysis of our previous LA-ICP-MS data to determine whether differences in the chemical composition of precious corals are statistically significant with an emphasis on Mediterranean C. rubrum and Pacific C. japonicum. We focused on these two species because of (1) their historical interest, (2) their distinct geographic origins, (3) the fact that they both can show highly saturated red colour (keeping in mind that other species such P. elatius can have a similar colour) and (4) their economic significance (considering that C. japonicum fetches the highest prices in today's markets). We also focused on C. rubrum and C. japonicum corals because they represent the largest number of specimens that we had studied, providing greater reliability of the statistical analysis. In addition, preliminary results for other precious coral species from the Pacific Ocean (P. elatius and P. konojoi) are briefly discussed.

MATERIALS AND METHODS

The present-day or recent (less than about 100 years old) skeletons of C. rubrum used for this study came from the rocky coasts of the Mediterranean Sea in Algeria, Italy, France and Spain. The long-dead C. rubrum samples came from the Sciacca banks of Sicily, Italy (this material is hereafter referred to in this article as 'Sciacca coral'). Concerning Pacific samples, colonies of P. elatius and C. japonicum came from various locations in Tosa Bay (off Shikoku Island, Kochi Prefecture, Japan). Additional specimens of P. elatius and C. japonicum of unknown origin and harvested before 2016 were obtained from a jeweller's private collection. Descriptions of these samples and their localities are provided in Vielzeuf et al. (2018) and Ricolleau et al. (2019). In addition, three cabochons—one each of C. rubrum, C. japonicum and Sciacca coral (Figure 3) of certified origin, were provided by the Antonino de Simone SRL coral factory in Torre del Greco, Italy. These three samples were analysed for this study to test the applicability of the proposed technique on polished, jewellery-quality samples. LA-ICP-MS analyses were performed on these three cabochons and compared with our previously published data, as a test of the discriminating method and as a demonstration of the feasibility and the minimally destructive character of the technique.

The trace-element analyses were obtained at Laboratoire Magmas et Volcans (Université Clermont Auvergne, Clermont-Ferrand, France) on an Agilent 7500cs inductively coupled plasma mass spectrometer (ICP-MS) coupled to a Resonetics M-50-E 193 nm excimer laser ablation system with maximum laser fl of 2.8 J/ cm^2. Analyses were made with a laser pulse frequency of 2 Hz and a beam diameter of 40 µm. The ablated material was carried by helium (0.7 l/min) and then mixed with nitrogen (1.5 ml/min) and argon (0.9 l/min) before entering the ICP. The following isotopes were measured: ^{7}Li, ^{23}Na, ^{24}Mg, ^{31}P, ^{55}Mn, ^{66}Zn, ^{88}Sr, ^{137}Ba, ^{208}Pb and ^{238}U, with integration times varying between 30 and 200 ms depending on the element and the session. Typical minimum detection limits (in ppmw or µg/g) were Li = 0.04, Na = 0.3, Mg = 0.2, P = 4.5, Mn = 0.7, Zn = 0.2, Sr = 0.02, Ba = 0.12, Pb = 0.02 and U = 0.01. The mean Ca abundance measured by electron microprobe for each coral species was used as an internal standard and NIST 610 glass was used as an external standard (Gagnon et al. 2008). The glasses NIST 612 and BCR-2G (Gao et al. 2002) were analysed to check the accuracy and precision of the analyses. A typical signal

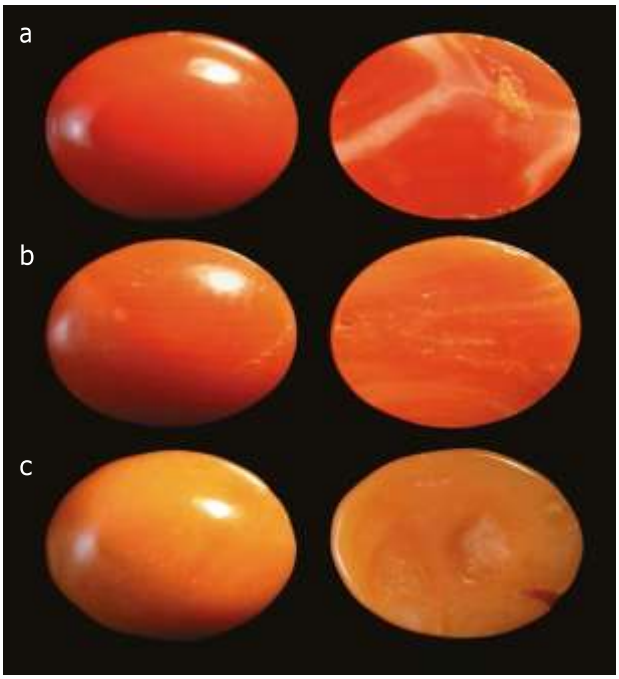

Figure 3: Three coral cabochons of known origin were analysed for this study, and each is shown here from the top and bottom: (a) C. japonicum (0.24 g; 9.4 × 7.0 × 2.7 mm), (b) C. rubrum (0.21 g; 9.0 × 7.0 × 2.4 mm) and (c) C. rubrum Sciacca coral (0.24 g; 8.7 × 6.7 × 3.0 mm). Samples courtesy of Antonino de Simone SRL; composite photo by D. Vielzeuf.

acquisition consisted of collecting a background signal for 30 s followed by the laser firing for 70 s. Trace-element reductions were done with Glitter software (Van Achterbergh et al. 2001).

Because analyses were obtained during different sessions, care was taken (1) to analyse the same sample of C. rubrum (from the Medes Island, Spain) at the beginning of each session to check for analytical consistency, and (2) to use similar instrumental configurations that ensure the reproducibility of the analyses from one session to another. During the analytical process, the signal stability was monitored to identify potential anomalies (e.g. holes or foreign material in the coral). The samples (other than cabochons) were cut perpendicular to the main axis of the coral branch, with or without removal of the dried organic tissues, and mounted in epoxy and polished. The cabochons were analysed without any preparation. Five laser ablation spots were made on the flat base of each cabochon, in zones with the deepest colour. (The specific location of the analyses on the cabochons was probably of little importance, as we found previously that Ba and Pb concentrations are not significantly different in medullar and annular zones; Vielzeuf et al. [2018].) The analyses of the three cabochons (plus standards) were carried out by one of the authors (J-LD), and the 'blind' results were then transmitted to author DV for identification.

Statistical processing of the data, in particular using principal component analysis (PCA), was performed with R! software using the FactoMineR package (Lê et al. 2008). PCA is a relevant statistical tool to determine whether populations can be distinguished, with a good degree of confidence, within a given set of data. Two-dimensional scatterplots and circles of elemental correlations demonstrate visually the organisation and clustering of the data and any correlation, inverse correlation or absence of correlation among variables (here, the concentrations of elements).

RESULTS AND DISCUSSION

Discriminating Elements

Figure 4 shows a two-dimensional scatterplot of the PCA results for 542 LA-ICP-MS analyses from 20 samples of C. rubrum and 281 analyses from 11 samples of C. japonicum. Among the analysed elements, concentrations of seven of them (Li, Na, Mg, Sr, Ba, Pb and U) were reduced to two new variables (principal components PC1 and PC2) that were computed to preserve the maximum amount of information and investigate

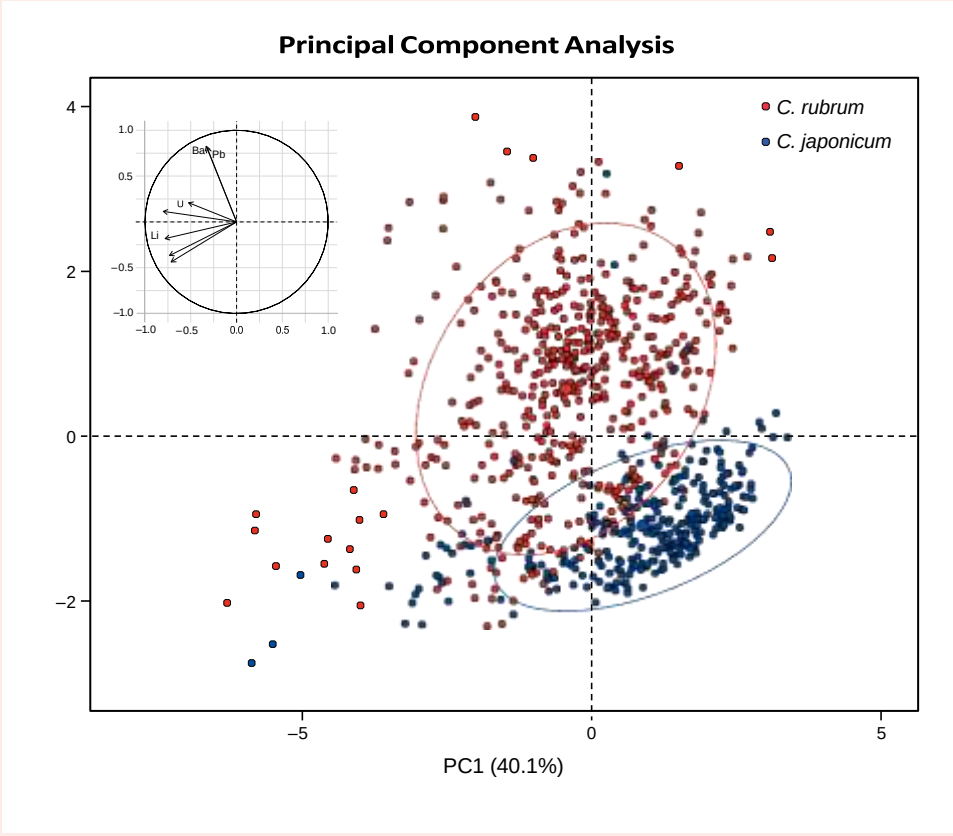

Figure 4: Application of principal component analysis to the concentrations of selected elements (Li, Na, Mg, Sr, Ba, Pb and U) in recent *C. rubrum* and *C. japonicum* samples from the authors' previous studies shows that these two corals have broadly different compositions. The circle of correlations (inset) shows excellent correlation between Ba and Pb and between Mg and Na.

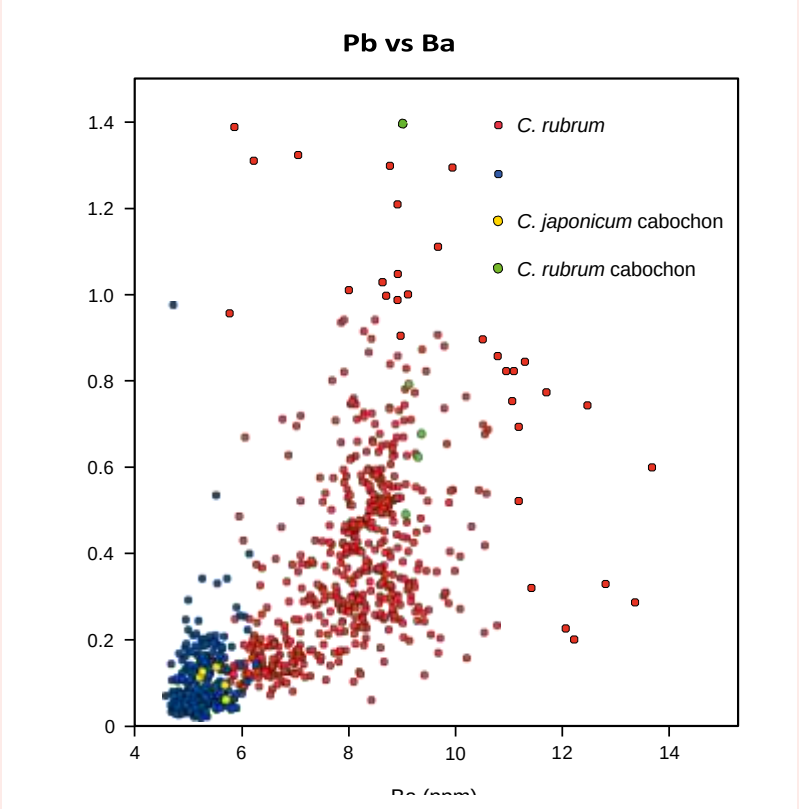

Figure 5: This diagram plots Pb vs Ba for *C. rubrum* and *C. japonicum* corals from the authors' previous research and for two of the cabochons analysed for the present study. Data from Sciacca corals are not plotted on this diagram because Sciacca corals can show significant differences in Pb concentrations compared to present-day *C. rubrum* (Ricolleau *et al.* 2019).

of Mn will be discussed separately below.) Figure 4 shows an obvious clustering of the two groups with limited overlap of the C. rubrum and C. japonicum domains, meaning that the two populations have statistically different compositions overall. The percentage values shown on the x and y axes indicate how much of the variance in the original dataset is explained by each principal component axis. In the present case, PC1 and PC2 account for or 'explain' 40.1% and 25.1% of the overall variability of the data, respectively. Therefore, the explanation rate of the total variance by the two components exceeds 65%.

The circle of correlation in Figure 4 (inset) is a tool to explain the significance of the two principal components. A coincidence of vector direction for two elements indicates a perfect correlation between them. Opposite directions (180°) mean the elements are inversely correlated, while vector directions at 90° point to an absence of correlation between the two elements. Also, the vector length is an indication of the importance of the element in the PCA. In Figure 4, the circle of correlation indicates that Mg and Na, and to a lesser extent Sr, Li and U, are positively correlated with one another (and inversely correlated with Ca and S, not shown here but demonstrated by Vielzeuf et al. 2018). Furthermore, the vector direction for these elements indicates that they are responsible for the variation along the PC1 axis. This variability —in other words, variations in Mg and Na (and, somewhat, in Sr, Li and U)— can be attributed to differences in growth rate both between annular and medullar zones and within growth rings in Corallium skeletons (see Vielzeuf et al. 2018 for an extended discussion). The circle of correlation in Figure 4 also shows a strong positive correlation between Ba and Pb in the PC2 vector direction, and no correlation between these two elements and the previous group of elements (Mg and Na). Thus, Ba and Pb are responsible for the variations along the PC2 axis and favour the separation between the C. rubrum and C. japonicum populations in Figure 4.

This observation led us to plot the data into a binary Pb vs Ba diagram (Figure 5), which shows that the domains of C. rubrum and C. japonicum overlap only slightly, with Ba and Pb concentration boundaries at 6 and 0.2 ppm, respectively. Indeed, 96% of the C. rubrum analyses have Ba contents >6 ppm and 98% of the C. japonicum analyses have Ba ≤6 ppm. In addition, 77% of the C. rubrum analyses have Pb contents ≥0.2 ppm and 94% of the C. japonicum analyses have Pb <0.2 ppm. These critical values could change slightly as more data become available. These observations agree with the potential of Ba as a strong indicator of the geographic origin of precious corals, as previously proposed by Hasegawa et al. (2012) and Vielzeuf et al. (2018).

The differences in Ba and Pb concentrations in Corallium species from the Pacific Ocean and the Mediterranean Sea can be attributed to the fact that the Mediterranean Sea is a relatively small and closed sea in which concentrations of these elements are higher than in the Pacific Ocean (Lea & Boyle 1991; Ricolleau et al. 2019). We carried out a similar statistical analysis on different species of precious corals from the Mediterranean Sea (C. rubrum) and Pacific Ocean (C. japonicum, P. elatius and P. konojoi; see diagram in The Journal's online data depository). The results show that the Ba and Pb contents of the different Pacific species are too close to distinguish them from each other. Because some pink-to-red corals from the Pacific Ocean are included in CITES Appendix III (i.e. those listed in Table I, as well as P. secundum) —while C. rubrum is not— it is most important to know whether coral species fished from the Pacific Ocean have a different chemical signature than C. rubrum from the Mediterranean Sea. We did not observe any relationship between colour and Ba or Pb contents in the precious corals we studied, so the chemical fingerprinting method that we propose can be applied to samples encompassing a wide range of colour, from white to pink to deep red.

To summarise, in all these precious corals, we attribute PC1 variations to differences in the growth rates in the skeletons, and we assign PC2 variations to differences in element concentrations between the Mediterranean Sea and Pacific Ocean. The circles of correlations indicate that the most important elements associated with PC1 are Mg and Na, while those associated with PC2 are Ba and Pb.

We therefore carried out additional PCA statistical processing on the same database taking into consideration only the four elements Mg, Na, Ba and Pb. Figure 6 shows that the C. rubrum and C. japonicum ellipses containing 75% of the data do not overlap and that the explanation rate by the two components rises to 77% (rather than 65%).

The elements Sr, Li and U occupy an intermediate position in the circles of correlation, which could indicate that their variations in the coral skeletons are due not only to growth rate factors, as proposed by Vielzeuf et al. (2018), but also to slight differences in composition, with those from the Mediterranean Sea being slightly richer in these elements than those from the much larger Pacific Ocean. Further work is needed to verify this correlation.

Sciacca Coral

Based on unpublished data mentioned in Rajola (2012) and on further analyses of Sciacca red corals, Ricolleau et al. (2019) noted that these long-dead C. rubrum corals have slightly lower concentrations of Na, slightly higher concentrations of U and Cu, and much higher concentrations of Mn and Fe than present-day (or recent) samples. We have previously proposed that reducing conditions might have existed in the organic-rich sediments surrounding the dead corals, such that the oxidation states of Mn and Fe changed, allowing these elements to enter the calcitic skeletons (Ricolleau et al. 2019). The above-mentioned elements, and especially Mn, could be indicators of diagenetic transformations in the red coral and a distinctive feature of Sciacca versus present-day (or recent) Mediterranean C. rubrum. The mean Mn contents in non-Sciacca C. rubrum and C. japonicum are both close to 1 ppm (Vielzeuf et al. 2018). Based on presently available data, we consider that Mn contents greater than 10 ppm indicate diagenetic transformations that affected long-dead Sciacca precious corals. To the authors' knowledge, chemical data for long-dead precious corals from the Pacific Ocean are not yet available. It would be interesting to check if the chemical features observed in the Sciacca C. rubrum samples also apply to long-dead precious corals from the Pacific Ocean.

Results of Blind Testing on the Cabochons

The LA-ICP-MS technique proved to be minimally destructive, as the craters from the analyses were hardly visible on the back surfaces of the cabochons, even under magnification. Chemical data for the three cabochons are listed in Table II. On the basis of the criteria of Ba >6 ppm and Pb >0.2 ppm for distinguishing C. rubrum corals, analyses 8, 11, 14, 21 and 24 were identified as C. japonicum, and all other analyses came from the two C. rubrum cabochons (i.e. Sciacca and present-day or recent coral). The Mn contents in analyses 10, 13, 16, 23 and 26 were approximately 20 times higher than in analyses 9, 12, 15, 22 and 25, which allows the separation of the Sciacca cabochon from the present-day or recent C. rubrum sample. In addition, the Na and U contents in the Sciacca corals are, respectively, lower and higher than in the present-day corals (see Table II), as expected from the trends noted by Ricolleau et al. (2019). Using

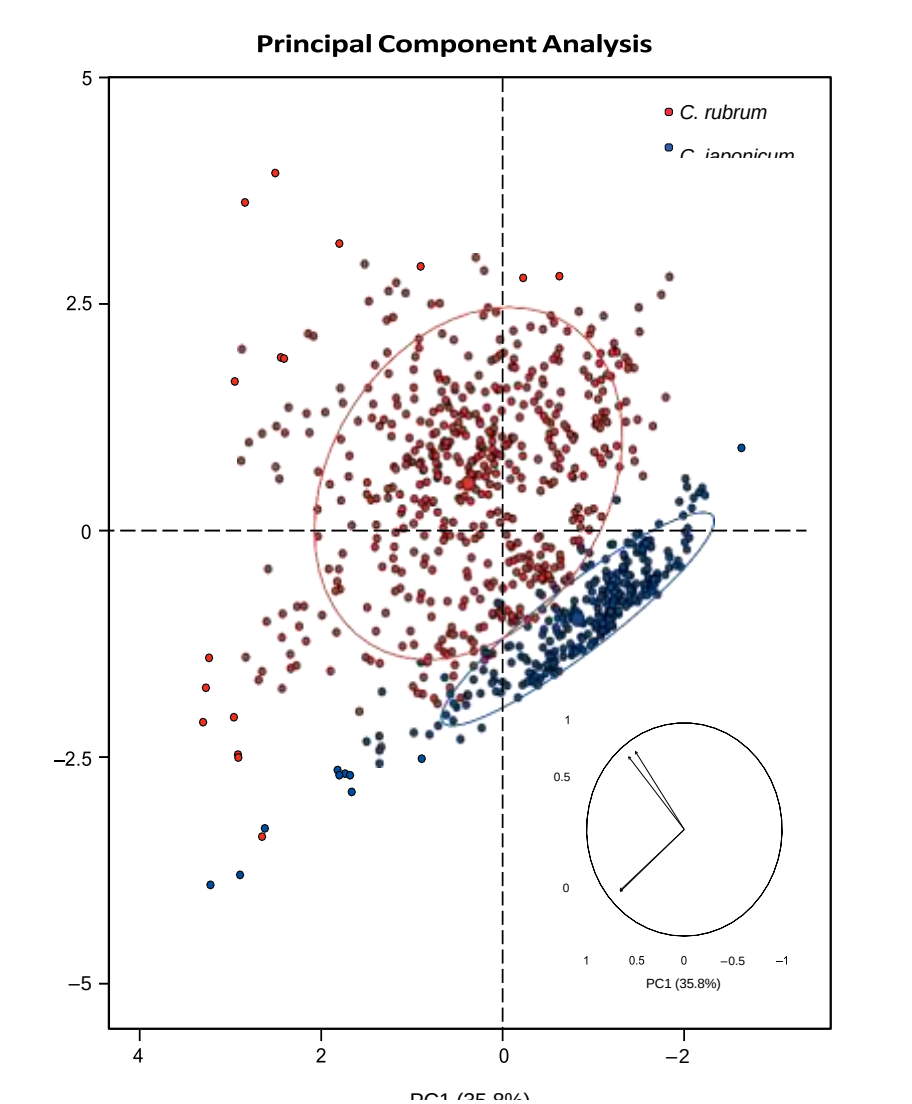

Figure 6: Principal component analysis taking into account the elemental concentrations of only Na, Mg, Pb and Ba shows a distinct clustering of the data for *C. rubrum* and *C. japonicum* corals.

these criteria, all three cabochons were correctly identified. The data for the C. japonicum cabochon and the present-day or recent C. rubrum sample are plotted in Figure 5. Data for the Sciacca cabochon are not included in this figure because Sciacca coral can show significant differences in Pb concentrations compared to present-day corals (see below and Ricolleau et al. 2019).

Suggestions for a Protocol

To determine the provenance of polished corals of unknown origin using LA-ICP-MS chemical analysis, two protocols can be followed: (1) analyse the samples and compare them to data from the present study by plotting the unknowns in the Pb vs Ba diagram, or (2) analyse known samples of C. rubrum and C. japonicum and use them as standards to compare with samples of unknown origin. The second protocol allows more accurate determinations, as it avoids comparison of data obtained with different instruments and analytical configurations. As discussed above, the use of a limited number of elements (i.e. Mg, Na, Ba and Pb) could prove more efficient in discriminating populations of precious corals than using all elements commonly measured by LA-ICP-MS. We suggest analysing at least five spots on each sample to assess for any anomalous compositions and to

reach a robust conclusion. We expect the concentrations of Ba and Pb in a given sample to be insensitive to the specific location of the analytical spot or variations of colour.

Limitations and Comparison with Other Methods

From a logistical standpoint, a standard LA-ICP-MS sample chamber can accommodate samples up to 17 × 13 × 2.2 cm.

Table II: LA-ICP-MS analyses (in ppm) of three coral cabochons: C. rubrum, C. japonicum and Sciacca (long-dead C. rubrum).*

Analysis no.	Li	Na	Mg	P	K	Mn	Sr	Ba	Pb	U	Identifi
08	2.5	3726	30023	194	111	0.9	2653	5.2	0.11	0.08	*C.japonicum*
11	2.6	3822	29929	204	118	<0.6	2644	5.3	0.13	0.06	*C.japonicum*
14	2.3	3442	28642	234	122	<0.7	2530	5.7	0.10	0.05	*C.japonicum*
21	2.6	3656	30171	223	113	1.0	2660	5.7	0.06	<0.03	*C.japonicum*
24	2.5	3552	29117	197	113	0.8	2533	5.5	0.14	<0.03	*C.japonicum*
09	3.0	3694	26477	118	127	<0.6	2766	9.1	0.49	0.08	*C.rubrum*
12	3.1	3645	27567	202	124	0.9	2754	9.1	0.79	0.06	*C.rubrum*
15	3.5	4109	28166	169	137	1.1	2779	9.3	0.62	0.13	*C.rubrum*
22	4.7	4853	29776	177	157	0.7	2950	9.4	0.68	0.10	*C.rubrum*
25	2.4	3187	25692	202	130	1.2	2648	9.0	1.40	0.07	*C.rubrum*
10	2.1	3069	24792	170	141	22	2683	10.1	0.69	0.22	*C. rubrum* (Sciacca)
13	2.5	3517	25461	189	145	22	2710	9.1	0.70	0.19	*C. rubrum* (Sciacca)
16	2.6	3371	26215	166	135	17	2677	9.2	0.72	0.15	*C. rubrum* (Sciacca)
23	2.4	3231	26351	168	131	17	2690	8.7	0.68	0.18	*C. rubrum* (Sciacca)
26	2.3	3215	26657	168	135	20	2746	8.4	0.77	0.15	*C. rubrum* (Sciacca)

* The shaded data show the trends of higher Ba and Pb in C. rubrum than in C. japonicum corals. In addition, Sciacca corals are enriched in Mn and contain slightly more U and less Na (on average) than present-day or recent C. rubrum skeletons.

This may be problematic for larger-sized coral carvings, and also for some objets d'art containing coral, as well as some necklaces (e.g. those with coral set in non-articulated metalwork), although special sample chambers are available that can accommodate objects greater than 20 cm in diameter and 12 cm in height.

As with any other discriminating method, applying chemical criteria has some limitations. Although Ba contents are constant within a given coral colony (i.e. no differences between medullar and annular zones) and are stable over time (Ricolleau et al. 2019; Vielzeuf et al. 2018), one study has shown that Ba concentration in Japanese precious corals increases at ocean depths below about 300 m (Yoshimura et al. 2015). Thus, deep-water red Japanese corals might attain Ba contents similar to those of near-surface Mediterranean corals. Further studies are needed to determine if, under

extreme circumstances, Ba contents in Mediterranean and Pacific corals overlap. Concerning Pb, Ricolleau et al. (2019) showed that Corallium skeletons are proxies of the Pb content in seawater and may show enrichment correlating to peak lead pollution during 1970–1990. Thus, it should be kept in mind that Pb concentrations in precious corals can vary with time and space. Nevertheless, despite these caveats, our studies demonstrate that the discriminating factors we determined are statistically robust.

Characteristics of the organic matrix in the axial skeleton of precious corals are species-specific and also could be used as an identification tool. However, this has been investigated in only a single study that included a limited number of species (Debreuil et al. 2011), and so far this method has not been shown to be a standardised or easy-to-use tool (Ledoux et al. 2016; Lendvay et al. 2020). Recently, some studies have explored the identification of precious coral species using DNA-based techniques. DNA sequencing methods are promising, but they are easier to implement on soft tissues than on coral skeletons (del Gaudio et al. 2004; McFadden et al. 2006; Uda et al. 2011, 2013; Ledoux et al. 2013). Moreover, DNA extraction from soft tissues is not feasible when working with processed pieces of precious coral. Cartier et al. (2018) proposed DNA analysis as a tool in gemmology to distinguish coral species, but noted that DNA fingerprinteg required significant amounts of sample material and was difficult to apply on items that cannot be destructively tested. More recently, Lendvay et al. (2020) tested different DNA extraction methods to produce high-purity DNA in sufficient quantities from minimal amounts of skeletal material. These authors amplified and sequenced the recovered DNA, and taxonomically identified coral samples through mitochondrial barcoding markers. With this method, C. rubrum could be unambiguously distinguished from C. japonicum when sufficient skeletal sample material was used. The method was 100% accurate when 100 mg (equivalent to 0.5 ct) of coral was used, but the success rate declined to 64% with a sample size of only 2.3 mg (about 0.01 ct).

Figure 7: The Mediterranean coral in this bracelet consists of a naturally closed central branch and 3-mm-diameter beads. Photo courtesy of Antonino de Simone SRL.

CONCLUSIONS

The development of advanced analytical methods is needed to aid in the identification of biogenic gem materials and to separate CITES-listed coral species from those not listed by CITES, in order to address fraud and illegal trading (Cartier et al. 2018). The chemical fingerprinting method proposed in this article proved successful for separating C. rubrum (e.g. Figure 7) from C. japonicum precious corals. More generally, the method allows separation of polished coral specimens from the Pacific and Mediterranean regions. Indeed, an important conclusion of this work is that the primary factor controlling the concentrations of Ba and Pb in the skeletons of precious corals is not the species itself but the composition of the seawater in which it grew. Barium and Pb are of critical importance in marine environments, and therefore this chemical fingerprinting method has implications for scientific disciplines as disparate as gemmology, archaeology, economics, marine ecology, and climate and environmental sciences. Regarding the gemmological implications, it must be remembered that identifying a sample as C. japonicum does not automatically mean that it is protected by CITES. If such a sample was fished before the species was included in CITES, then it can be traded. Furthermore, samples identified as C. rubrum can be freely traded since they are not protected by CITES.

Compared to other advanced analytical techniques, and especially to DNA fingerprinting, the statistically tested chemical fingerprinting method presented here (1) is relatively easy to implement; (2) is minimally destructive, as extremely small amounts of material (~2×10^{-4} mg or ~4×10^{-5} ct) are required per analysis; (3) does not require any special preparation of samples; (4) is based on LA-ICP-MS equipment found in several well-equipped gemmological laboratories; and (5) is efficient and relatively affordable, as tens of samples can be analysed in a single day. As such, the method proposed in this article can contribute to the enforcement of international CITES regulations and national laws, and thus to the preservation of the always exquisite Corallium species.

Acknowledgements

This work was supported by the Centre National de la Recherche Scientifique (CNRS), the Institut National des Sciences de l'Univers (INSU) and the Agence Nationale pour la Recherche (ANR) through ANR MOBi 2018-2021. This study benefitted from the generosity of numerous contributors who supplied samples. We thank P. Raffin, J. G. Harmelin, J. Garrabou, N. Yahiaoui, F. Costantini and C. Marschal for providing C. rubrum samples from various places in the Mediterranean region. G. Rajola (Torre del Greco, Italy) supplied some Sciacca samples, while Antonino de Simone SRL (Torre del Greco) provided the cabochons. Samples of C. japonicum, C. elatius or C. konojoi were kindly provided by S. Tambutté of the Centre Scientifi de Monaco (CSM) and G. Tanaka of the Precious Coral Protection and Development Association of Japan. We also thank K. Saiki of Osaka University for establishing our fruitful exchange with G. Tanaka. Comments from three anonymous reviewers were also helpful. This is contribution ANR MOBi no. 3.

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