

1 **Origin of bluish pectolite aka larimar from the Dominican Republic:**

2 **Constraints from Mineralogy and Geochemistry**

3
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17 18 19 20 **Abstract**

21 The commonly known larimar is usually a gem-quality, bluish pectolite ($\text{NaCa}_2\text{Si}_3\text{O}_8\text{OH}$),
22 intergrown with other associated phases such as natrolite, prehnite, calcite, chlorite, found
23 only in the Dominican Republic. Less frequently it shows consecutive and/or sequential
24 green, blue, and white coloration within single amygdales/veins developed in altered
25 (chloritized, serpentinized) Cretaceous basalts of the Dumisseau Formation. The origin of
26 larimar is linked to the circulation of low-temperature (<170 °C) alkali-rich deuteric fluids
27 that were later mixed with meteoric waters. Variations of CL colors, ranging from weak
28 brown in green pectolite to strong yellow (Mn^{2+} -activated) in blue and white species, were
29 ascribed to the transition from oxic to suboxic crystallization environment within the single

30 larimar bodies. These changes could be induced by the burial of magmatic rocks and resulted
31 in the emergence of early zeolite (natrolite), and subsequent formation of native copper in a
32 sulphur-deficient hydrothermal environment. Pectolite-forming elements (e.g. Ca and Na),
33 followed by such transition metals as Cu, Cr, Co, and Ni, were released via the alterations of
34 magmatic phases (diopside, aegirine-augite, and chromite-magnetite) and/or leached from
35 basaltic groundmass. Decoupling between $\delta^{18}\text{O}$ values of blue (up to 10.67‰), green (up to
36 9.66‰), and white pectolite (up to 15‰) was maintained by a progressive temperature drop
37 during ongoing pectolitization and/or presence of the boiling-related environment.
38 Meanwhile, anomalously low δD values (from -390.51‰ to -294.02‰) indicate that the
39 crystal structure of pectolite tends to incorporate light hydrogen isotope regardless of the
40 original δD values in mineralizing fluids.

41

42 **Keywords:** Dominican Republic, larimar, pectolite, native copper, cathodoluminescence
43 (OM-CL), isocon diagrams, deuterium alterations

44

45 1. Introduction

46 The term “larimar” was coined in the mid-1970s and corresponds to the unique,
47 massive, bluish, and gem-quality variety of pectolite, i.e. a member of wollastonite-group
48 species (Prewitt and Buerger, 1963) with a general formula of $\text{NaCa}_2\text{Si}_3\text{O}_8(\text{OH})$. Its coloration
49 varies from blue to greenish, often streaked with white patterns that locally form a distinctive
50 polygonal pattern. Larimar, known also as a blue gem of the Caribbean, occurs solely on the
51 Barahona Peninsula, in the southwestern part of the Dominican Republic (Woodruff and
52 Fritsch, 1989). It mostly appears as nodules, veinlets, and/or irregular impregnations within
53 host rocks involving Cretaceous magmatic extrusives (basalts, dolerites) and corresponding
54 pyroclastic deposits (i.e. spilite tuffs), though common examples of pectolitized tree trunks

55 have been also frequently reported (Espí and Pérez-Puig, 2009; Kowalczyk-Szpyt, 2020;
56 Wagner et al., 2017; Woodruff and Fritsch, 1989). The pectolite can be found there in close
57 association with calcite, prehnite, zeolite, and/or SiO₂-group minerals (Bente et al., 1991;
58 Broda et al., 2022).

59 The latest studies on larimar have mainly focused on the origin of its unique blue-
60 green coloration, which is considered a worldwide phenomenon. According to Kloprogge et
61 al. (2016), the presence of (Pb-Pb³⁺) pairs can be responsible for the blue-green color of
62 pectolite from the Dominican Republic, although Bente et al. (1991) and also Woodruff and
63 Fritsch (1989) argue for the presence of V³⁺ and Cu²⁺ impurity centers, respectively. The very
64 recent study of Huang et al (2023) showed the substitution of V⁴⁺ and Fe²⁺ for Ca²⁺ as well as
65 the orientation of pectolite fibers can also act as a coloration mechanism in larimar. The
66 formation conditions of pectolite mineralization remain vague and have not been
67 reconstructed in detail yet. However, it is accepted that this gemstone is of hydrothermal
68 affinity and might have formed in temperature conditions that did not exceed 240 °C (Bente et
69 al., 1991).

70 Nonetheless of the limited abundance of larimar around the globe, pectolite is a fairly
71 common hydrothermal (mostly low-temperature) phase found in vugs and fissures among
72 volcanic rocks such as basalts and dolerites (Jelínek et al., 1980). It has also been encountered
73 among debris flows (Craw and Landis, 1980), kimberlites (Weska et al., 2020), and rodingites
74 (Wenner, 1979). The crystallization of pectolite may reflect the influx of late-stage Ca-Na-
75 bearing fluids under near-surface conditions and/or along the zones with reduced pressure and
76 very low CO₂ concentration in the system (Włodyka and Wrzalik, 1999). Otherwise, it can be
77 of hydrothermal-metasomatic (replacive) affinity (e.g. after plagioclase), as has been reported
78 by Włodyka and Wrzalik (1999) and Wilshire (1967). Finally, following Carr et al. (1976),
79 primary pectolite can even crystallize from residual Na-bearing and Si-poor phonolitic melts.

80 In this paper, the new findings on the poorly understood formation history of the
81 multi-colored pectolite (larimar) from the Dominican Republic are provided. Particularly,
82 combined electron-microprobe (EMPA) and cathodoluminescence studies (OM-CL),
83 supported by O-H isotopic measurements and chlorite thermometry, have been used to
84 determine the source and temperature of pectolite-forming fluids, as well as to establish the
85 potential changes of physicochemical conditions during the formation of green, blue, and
86 white pectolite species found within the single larimar bodies. Additionally, we aim to
87 determine the mobility of main and trace elements during incipient pectolitization (using the
88 so-called isocon diagram) based on whole-rock major and trace element data of strongly
89 altered (e.g. chloritized and zeolitized) larimar-bearing and larimar-poor volcanics. Finally,
90 mechanisms of precipitation of native copper, found in association with blue pectolite, and
91 potential sources of Cu-bearing fluids were discussed.

92

93 **2. Geological background**

94 The Las Filipinas larimar deposit, covering about 32 ha, is located on the hill in the
95 Sierra de Bahoruco Mountain range, at an altitude of 750 m above sea level. It is near the
96 town of Los Chupaderos, about 15 km south-west of Barahona city (the Barahona Province)
97 in the south-west of the Dominican Republic (Fig. 1a-c). The region is a part of the Hotte
98 Selle Bahoruco oceanic plateau terrane (Draper et al., 1994; Espí and Obieta, 2017). It is
99 dominated by the Neiba Formation, aged Eocene to Lower Miocene, and composed of fine-
100 crystalline, red-algae, pelagic limestones underlain by volcanics of the Dumisseau Formation
101 (DFm) associated with suboceanic magmatism of Cretaceous age (Escuder-Viruete et al.,
102 2016; Loewen et al., 2013; Sen et al., 1988; Whattam and Stern, 2015). The DFm is
103 interpreted as an emerged fragment of the Caribbean Large Igneous Province (CLIP), formed
104 by the emplacement of mafic magmas above a mantle plume (Escuder-Viruete et al., 2016).

105 The DFm consists of the 1500 m section of massive and pillow basalt and picrite
106 flows, with pyroclastic deposits, all locally intruded by dolerite dykes and sills (Escuder-
107 Viruete et al., 2016, 2009). Escuder-Viruete et al. (2016) described three types of volcanic
108 facies in this region, i.e. (1) coherent, mafic flows and autoclastic breccias, (2) mafic breccias
109 and tuffs formed by subaqueous eruptions, and (3) re-sedimented syneruptive polygenetic
110 breccias with fine-grained volcanoclastics. Based on the whole-rock geochemistry,
111 specifically TiO_2 content and incompatible trace elements, Escuder-Viruete et al. (2016)
112 distinguished three groups of basaltic rocks there, i.e. low-Ti tholeiites (I group), high-Ti
113 transitional basalts (II group), and high-Ti, LRRE- rich alkaline basalts (III group), which
114 represent aggregate melts produced by progressive decompression melting in mantle plume.
115 The $^{40}\text{Ar}/^{30}\text{Ar}$ ages obtained for altered basaltic rocks from the DFm in the Sierra de Bahoruco
116 indicated the extrusive activity *ca.* 74.2 ± 1.7 Ma ago (Late Campanian), whereas the ages of
117 *ca.* 52.8 ± 1.5 Ma for unaltered dolerite dyke, intersecting the volcanic facies, showed the
118 formation of transitional magmas until Lower Eocene (Escuder-Viruete et al., 2016). Both
119 older and younger magmas are geochemically and isotopically the same, proving the same
120 plume-influenced mantle source and the prolonged volcanism in the CLIP (Escuder-Viruete et
121 al., 2016). Later, all volcanic facies were affected by post-magmatic, hydrothermal alteration,
122 which led to the formation of unique blue-green-white, gem-quality pectolite, associated with
123 natrolite and calcite, forming veins, patches, and nests within basalts and pyroclastic rocks. At
124 the contact of basaltic rocks with pyroclastic deposits (Fig. 2a-b) there are the charred
125 remnants of seasonal tropical trees, mainly trunks, roots, and branches, also strongly altered as
126 a result of hydrothermal activity (Wagner et al., 2017; Woodruff and Fritsch, 1989).

127 **3. Material and methods**

128 Three color varieties of pectolite including green-, blue-, and white-colored species
129 (marked throughout the entire text as Pct-I, Pct-II, and Pct-III, respectively), along with the
130 host basaltic rocks from the Las Filipinas deposit (see Fig. 2a-b), have been examined in the
131 following study. The samples for the studies were collected by Carlos George (the co-author
132 of the article).

133

134 3.1. Optical microscopy and cathodoluminescence

135 Thin sections of larimar and host basalts were analyzed with Olympus BX 51
136 polarizing microscope with a magnification ranging from 40× to 400×, using both transmitted
137 and reflected light modes. The photomicrographs were acquired using an Olympus DP12
138 digital camera equipped with the Analysis software. The optical cathodoluminescence (OM-
139 CL) observations were conducted on polished thin sections using ZEISS polarizing
140 microscope linked to the CITL Mk5 cold-cathode CL device, which operated at the following
141 conditions: 10-15 kV accelerating voltage, ca. 300-400 mA current, and 0.003-0.005 mbar
142 vacuum. Photomicrographs were recorded by a Canon camera attached to the microscope. CL
143 spectra were collected using LEO 1430 scanning electron microscope with a CL-image
144 system (ASK-CL VIS View) and CL spectrometer (ASK SEM-CL). The system operated in a
145 high-vacuum mode, at 20 kV accelerating voltage, and 50 μA current. The intensity of
146 recorded CL spectra was normalized to 100% in terms of the intensity units.

147 3.2. Scanning Electron Microscopy

148 Back-scattered electron (BSE) observations were conducted on both rough samples (to
149 describe the morphology and size of individual crystals) and thin sections (to identify
150 accessory phases coexisting with pectolite) using an FEI Quanta 200 FEG scanning electron
151 microscope equipped with an EDAX energy dispersive spectrometer (EDS). The system

152 operated at 25 kV accelerating voltage, 50 μ A current, in a high-vacuum mode, i.e. 6×10^{-5} -
153 7×10^{-6} Torr. The quantitative analysis of target elements, based on relative peak intensity
154 calculated from the EDS spectrum, was supported by ZAF correction.

155

156 3.3. Electron microprobe analyses (EMPA)

157 EPMA analyses of three color varieties of pectolite and main larimar-bearing rock
158 components, i.e. primary pyroxene and secondary chlorite, were performed with a JEOL
159 Super Probe JXA-8230 operating in a wavelength-dispersive (WDS) mode under the
160 following conditions: an accelerating voltage of 15 kV, a beam current of 20 nA, beam size of
161 2 μ m, a peak count-time of 20 seconds, and a background time of 10 seconds. The EMPA
162 standards, analytical lines, diffracting crystals, and mean detection limits for the elements are
163 presented in **Tab. 1**. The JEOL ZAF procedure was used for the matrix correction of the raw
164 data.

165

166 3.4. Oxygen and hydrogen isotope analyses

167 Stable hydrogen and oxygen isotopes were measured on isotope ratio mass
168 spectrometer (IRMS) MAT253, coupled to an elemental analyzer Flash2000 HT Plus
169 (Thermo Scientific). Pulverized mineral samples of 500-900 micrograms were wrapped into
170 silver capsules and pyrolyzed in glassy carbon tube at 1400°C. The product gas mixture was
171 separated on GC column (5Å mol sieve) to pure H₂ and CO that entered the IRMS via
172 continuous-flow interface and were measured against reference gases H₂ and CO. The raw
173 measurements were calibrated using international reference materials GISP (δ D = -189.70 ‰,
174 δ 18O = -24.78 ‰) and USGS50 (δ D = 32.80 ‰, δ 18O = 4.95 ‰). All values are reported in

175 permil vs. SMOW, with a measurement precision of ~1.7 ‰ for hydrogen and ~0.29 ‰ for
176 oxygen.

177

178 3.5. Whole-rock geochemistry

179 Two types of rock samples have been investigated, i.e. pectolite-rich and pectolite-
180 poor basalts, both showing a pronounced degree of secondary alterations involving e.g.
181 chloritization and serpentinization of mafic phases (e.g. olivine and pyroxene). Whole-rock
182 major and trace element analyses were conducted at Bureau Veritas Minerals Laboratories
183 Ltd. in Vancouver Canada, using the LF200 package. The material of 5g per sample was
184 crushed in an agate mortar and sieved before the analysis. Samples were then mixed with
185 $\text{LiBO}_2/\text{Li}_2\text{B}_4\text{O}_7$ flux. Crucibles were fused in the furnace. The cooled bead was dissolved in
186 ACS grade nitric acid and analyzed by combined ICP-OES (Inductively Coupled Plasma -
187 Optical Emission Spectrometry by Spectro Ciros Vision device) and ICP-MS (Inductively
188 Coupled Plasma - Mass Spectrometry by ELAN 9000 device) for major and trace elements,
189 respectively. Loss on ignition (LOI) was measured by igniting a sample split and measuring
190 the weight loss. The precision and accuracy based on replicate analysis of international rock
191 standards fall between $\pm 2-5\%$ for most trace elements and $\pm 1\%$ for major elements. For
192 detection limits of particular elements, the reader is referred to <https://www.bureauveritas.pl/>.

193

194

195 4. Results

196 4.1. Mineralogy and chemistry of pectolite

197 Various colored pectolite in the hues of green (Pct-I), blue (Pct-II) and white (Pct-
198 III) occurs in nodules and cavities, as well as veinlets intersecting strongly-altered (i.e.
199 chloritized, zeolitized, and serpentinized) basaltic rocks of the Dumisseau Formation (DFm)
200 in the Sierra de Bahoruco region (SW part of Dominican Republic). Pct-I usually occurs in
201 relatively minor amounts and can be found in the outermost regions of larimar-forming
202 bodies. Instead, Pct-II and Pct-III are more common and occupy the innermost parts of these
203 bodies (Fig. 3). The transition between Pct-I and Pct-II is sharp and well-visible, whilst Pct-II
204 and Pct-III types are either welded together to form thin alternating bands or appear as
205 discrete zones. Moreover, the inner region of larimar sometimes reveals a tiled/polygonal
206 pattern, similar to those reported e.g. in turquoise (Liu et al., 2020) and consisting of nest-like
207 blue (or green) domains (Pct-I or Pct-II) intersected by veins of white-colored pectolite Pct-
208 III.

209 The green variety of pectolite (Pct-I) appears as fibrous and bundle-like crystals
210 radiating towards the center of vugs found in the basaltic host (Fig. 4a). The bladed to needle-
211 like individuals reach 5-10 μm in length and 1-5 μm in width and are typically grouped in
212 compact spherulitic aggregates (Fig. 4b). This type is accompanied by numerous prismatic
213 crystals of zeolite species (i.e. natrolite) up to ca. 1.5 mm in length. At the contact of Pct-I
214 with the host basaltic rock the numerous iron oxides are observed (Fig. 4a). Pct-II forms not
215 only massive and irregular mass but also comprises tightly interlocked acicular crystals
216 intersecting at ca. 90° , which fairly resemble fine-felted micro-texture typical of serpentinite
217 (Fig. 4c). The single, bladed to needle-like crystals of blue pectolite, with sizes of 5-10 μm in
218 length and 1-3 μm in width, thus form a parallel and compact structure (Fig. 4d).
219 Noteworthy, there are several inclusions of native copper and chalcocite at the boundary
220 between Pct-I and Pct-II (Fig. 5a-b). The native copper forms elongated or isometric
221 individuals up to ca. 0.1 mm in size, whereas chalcocite appears as irregular grains up to 0.02

222 mm. Pct-III occurs as radial-shaped or massive crystals, which show quite higher interference
223 colors (i.e. second-order blue) in some places (Fig. 4e). Under SEM the rigid, bladed to
224 needle-like individuals, reaching sizes of 10 to 40 μm in length and 1-3 μm in width, form
225 poorly bounded, parallelly arranged aggregates (Fig. 4f). Overall, the individuals of Pct-I and
226 II appear to be similar in terms of size and shape (i.e. bladed to needle-like crystals, reaching
227 sizes of 5 to 10 μm in length and 1-5 μm in width), the crystals of Pct-III, though similar in
228 terms of shape, are slightly less compact and a bit larger.

229 The green pectolite variety (Pct-I) exhibits weak cathodoluminescence (CL) colors in
230 the shades of brownish yellow. On the contrary, both blue (Pct-II) and white (Pct-III) species
231 display strong bright yellow luminescence (Fig. 6a-b), which is similar to other species in
232 wollastonite-group minerals (Dumańska-Słowik et al., 2020). The CL spectrum for the green
233 species (Pct-I) consists of a broad signal centered around 608 nm and thus the proper
234 identification of luminescence activators is unreliable. Blue (Pct-II) and white pectolite (Pct-
235 III) with yellow luminescence show pronounced asymmetric bands with emission lines at ca.
236 570 and 580 nm, and 564 and 577 nm, respectively (Fig. 6). These lines can be attributed to
237 Mn^{2+} impurity (Ramseyer and Mullis, 2000) following Ca^{2+} - Mn^{2+} isovalent substitution
238 (Gorobets and Rogojine, 2002). The presence of an asymmetric band in the region 550-650
239 nm with two emission lines may indicate the substitution of Ca by Mn in at least two
240 structural sites in both, blue and white pectolite species (Gorobets and Rogojine, 2002).
241 Whereas the assignment of the weak bands at ca. 396 and 472 nm, though diagnostic of blue
242 species (Pct-II), is problematic due to scarce literature data. In analogy to diopside or
243 danburite these bands may be due to O^* centers, i.e. recombination of a free electron with an
244 O^- hole center (Gorobets and Rogojine, 2002).

245 The chemical compositions of pectolite (Tab. 2) are very close to its theoretical
246 formula (Deer et al., 2013). Only slight variations are found between the color varieties, i.e.

247 the green species (Pct-I) has the average formula of $\text{Na}_{0.96}\text{Ca}_{2.02}\text{Si}_{2.99}\text{O}_8(\text{OH})$; the blue one
248 (Pct-II) $\text{Na}_{0.97}\text{Ca}_{2.01}\text{Si}_{3.00}\text{O}_8(\text{OH})$; and white species (Pct-III) $\text{Na}_{0.97}\text{Ca}_{2.00}\text{Mn}_{0.01}\text{Si}_{3.00}\text{O}_8(\text{OH})$.
249 Interestingly, white pectolite is the most enriched in manganese (*av.* 0.22 wt.% of MnO). The
250 content of this metal decreases for blue species (*av.* 0.08 wt.%) to a complete absence in the
251 green variety of pectolite. Whereas vanadium, which may be responsible for the color of
252 pectolite, is found only in green (Pct-I; 0.02 wt.% V_2O_3) and blue species (Pct-II; 0.01 wt.%
253 V_2O_3). The green pectolite contains also trace amounts of iron (0.11 wt.% FeO) and
254 potassium (0.03 wt.% K_2O).

255

256 4.2. Petrography and mineral chemistry of basalt

257 Host basaltic rocks exhibit massive to vesicular, porphyric, and hipocrystalline micro-
258 textures. Herein, phenocrysts are chiefly represented by the relicts of mafic phases (pyroxene
259 and/or olivine) as shown by partially preserved six-sides and/or eight-side sections (now filled
260 with secondary products), respectively (Fig. 7a). Pyroxene species is mostly altered to
261 colorless or slightly pleochroic (i.e. greenish) chlorite-group species, though some crystals
262 were preserved from a pervasive chloritization. The pyroxene crystals are greenish to
263 brownish under PPL and either occur as individuals or envelop larger olivine phenocrysts
264 (Fig. 7b). Additionally, fine but fresh and elongated pyroxene microlites were found in the
265 groundmass of volcanics, where they occur in association with clay-group species (smectite-
266 group and/or illite/celadonite) – Fig. 7c. On the other hand, olivine has been entirely
267 transformed into serpentine-group minerals forming mesh (or hourglass) textures, as well as
268 chlorite-group species accompanied by some subhedral sieved-textured opaques. Both altered
269 pyroxene and olivine tend to be mantled by iddingsite (mixture of clay minerals and Fe
270 oxides) at contact with the larimar bodies. Opaques (in thin sections) are represented by
271 spinel-group species of chromite-magnetite solid solution series (Fig. 7c). Secondary vug-

272 filling phases of basaltic rocks involve not only pectolite but also minor prismatic zeolite-
273 group phases (natrolite) and abundant isometric calcite, as well as scarce copper sulfides.
274 Noteworthy, pectolite occurs in amygdales and veinlets within basaltic rocks, although some
275 crystals also occupy the innermost regions of resorbed/altered mafic phases (e.g. pyroxene)
276 (Fig. 7d). Accessory fine crystals of apatite are disseminated within the rock matrix and/or
277 form inclusions embedded within fresh pyroxene.

278 The composition of two pyroxene species, i.e. (1) microlites found in the groundmass,
279 and (2) individual subhedral crystals that were partially preserved from chloritization are
280 summarized in Tab. 3. Based on EMPA analyses it was found that clinopyroxene microlites
281 (1) disseminated in the basaltic matrix are enriched in CaO (15.99-21.37 wt.%) with some
282 elevated amounts of Na₂O (2.33-3.99 wt.%), showing intermediate composition between
283 augite and aegirine (Morimoto et al., 1988), with the average formula of (Ca_{0.78}Na_{0.21}K_{0.01})
284 (Ti_{0.12}Fe³⁺_{0.11}Mg_{0.72}Fe²⁺_{0.04})(Si_{1.85}Al_{0.05}Fe³⁺_{0.10})O₆. The aegirine-augite species, showing
285 compositional ranges of Jd_{8.1-12.0}Q_{65.6-80.2}Ae_{11.2-22.4} (Tab. 3, Fig. 8), is also marked by high and
286 variable contents of iron (4.81-12.03 wt.% Fe₂O₃; 0.00-2.59 wt.% FeO), elevated of titanium
287 (3.60-4.68 wt.% TiO₂) and high magnesium (12.30-13.34 wt.% MgO). Hence, it is
288 characterized by high values of Mg# (Mg²⁺/(Mg²⁺+Fe²⁺), which range between 0.90-1.00, and
289 low Al₂O₃ (1.13-1.49 wt.%).

290 The relicts of phenocrysts (2) contain relatively high contents of SiO₂ (48.71-50.83
291 wt.%), CaO (20.87-21.38 wt.%) and MgO (13.05-13.61 wt.%), while quantities of other
292 elements are relatively lower (Tab. 3), i.e. TiO₂ (3.52-4.60 wt.%), Fe₂O₃ (4.21-5.49 wt.%)
293 FeO (2.24-3.00 wt.%), Al₂O₃ (0.83-1.45 wt.%), and Na₂O (1.95-2.23 wt.%). The average
294 composition of phenocrystic pyroxene is (Ca_{0.85}Na_{0.15})(Ti_{0.11}Fe³⁺_{0.06}Mg_{0.74}Fe²⁺_{0.08})
295 (Si_{1.87}Al_{0.05}Fe³⁺_{0.08})O₆. The compositions of this species plotted on Quad-Jd-Ae diagram

296 (Morimoto et al., 1988) falls within the Quad field, near the borderline with aegirine-augite
297 field (Fig. 8), and correspond to diopside species (Fig. 9).

298 The fine-grained secondary (replacive) chlorite species are characterized by a high
299 content of Si (3.33-3.46 apfu) with subordinate tetrahedral Al (0.54-0.67 apfu), as well as high
300 Al^{VI}/Al^{IV} ratios of 1.32-1.76. In the octahedral sites, Mg (4.17-4.53 apfu) predominates of
301 Fe^{2+} (0.38-0.56 apfu), with high values of Mg#, i.e. $Mg/(Fe^{2+} + Mg)$, in the range of 0.88-0.92.
302 The sum of octahedral cations falls between 5.69-5.83 apfu with the octahedral vacancy in the
303 range of 0.17-0.31 apfu (Tab. 4). The content of alkalis in interlayer sites is variable and
304 ranges from 0.07-0.21 apfu. Following the classification scheme proposed by Zane and Weiss
305 (1998), based on $Mg + Fe > Al + \text{vacancy}$ as well as dominant octahedral cation, the chlorite
306 species belongs to Type I (trioctahedral) Mg-chlorite. Its composition is close to the
307 clinocllore end-member (Fig. 10) of clinocllore-daphnite series (Plissart et al., 2009).

308

309 4.3. Chlorite geothermometry

310 Chlorite crystallization temperatures, calculated based on empirical geothermometers
311 that utilize Al^{IV} contents combined with Fe/Fe+Mg ratios (El-Sharkawy, 2000; Jowett, 2021;
312 Kranidiotis and MacLean, 1987), cover the ranges of 138-169°C, 136-162°C, and 105-148°C,
313 respectively (Tab. 5). These values are fairly consistent with the results derived from the Al^{IV} -
314 based geothermometer (Cathelineau, 1988) that fall between 111-154°C. Following a semi-
315 empirical (graphical) approach, where the relationship between R^{2+} (sum of divalent cations)
316 and Si content in apfu units (Bourdelle and Cathelineau, 2015) is involved, the analyses of
317 Mg-chlorite roughly plot between 100 and 170 °C isotherms (Fig. 11). The obtained
318 temperatures can be still slightly underestimated due to the presence of alkalis (Ca+Na+K)
319 falling between 0.07-0.20 apfu, as well as the lack of knowledge of exact Fe^{2+}/Fe^{3+} ratios.
320 Meanwhile, alkali contents show a negative correlation with the sum of divalent cations

321 values ($R^2=0.69$). The presence of Na+K+Ca in the Mg-chlorite species is possibly related to
322 the remnants of clinopyroxenes and/or the occurrence of other low-temperature phases typical
323 of altered basaltic rocks such as illite or corrensite (Powolny et al., 2022; Shau et al., 1990).

324

325 4.4. Whole-rock major and trace element geochemistry

326 Whole-rock geochemical analyses of larimar-poor (LA-01) and larimar-bearing (LA-
327 02) samples are presented in **Tab. 6**. In general, the geochemical character of the larimar-poor
328 sample (LA-01) is quite consistent with LREE-enriched basalts reported for the DFm of the
329 Sierra de Bahoruco region (Escuder-Viruete et al., 2016). It shows ultrabasic character (i.e.
330 low SiO₂ of 37.25 wt.%; though the effects of secondary alterations have likely lowered the
331 original value) and metaluminous affinity. The larimar-poor rock is high in MgO (17.12
332 wt.%), FeO (11.16 wt.%), and CaO (12.06 wt.%), as compared with alkalis (Na₂O+K₂O; 2.39
333 wt.%). The contents of such transition metals as Ni, Cr, and Co are also high, i.e. 533, 705,
334 and 70.6 ppm, respectively. Trace element characteristics of both samples (i.e. LA-01 and
335 LA-02) are similar, involving steep and LREE enriched segments character with
336 $[LREE/HREE]_{CN}$ of 3.12, high Nb/Yb and Th/Yb ratios of 30.71 and 1.42, and high Nb/Y of
337 3.28. These features are consistent with alkali basalts (Pearce, 1996), but also reflect the OIB-
338 related affinity of the parental magma and were likely enhanced by the prolonged period of
339 plume-related activity in the Caribbean Large Igneous Province, as reported by Sen et al.
340 (1988), Loewen et al. (2013), and Escuder-Viruete et al. (2016).

341 4.5. Isotopic characterization

342 The results of oxygen and hydrogen isotopic composition of pectolite types, along
343 with host basaltic rock are summarized in **Tab. 7** (see also **Fig. 12**). Relatively low, but
344 constant $\delta^{18}O$ values (from +6.38 to +9.66‰, with a mean of +8.06‰) have been observed in

14

345 green species (Pct-I). Slightly higher, but still tightly clustered $\delta^{18}\text{O}$ values have been
346 measured in blue pectolite (Pct-II), i.e. ranging from +8.59 to +10.67‰ (with a mean of
347 +9.60‰). Otherwise, remarkable variations of $\delta^{18}\text{O}$ values, ranging between +6.00 and
348 +14.99‰, were noted for white species (Pct-III) and reflect the mode of its occurrence (Tab.
349 7). Relatively large and fan-shaped crystals of Pct-III exhibit high $\delta^{18}\text{O}$ values between
350 +13.55 and +14.99‰, whereas vein-like Pct-III crystals, found in a polygonal type of larimar
351 (see the sample in the upper left corner of Fig. 3), have their $\delta^{18}\text{O}$ values as low as between
352 +6.00 and +8.17‰.

353 Assuming the pectolitization of alkali basalts could proceed in a similar temperature
354 range as chloritization, the $\delta^{18}\text{O}$ composition of larimar-forming fluids was calculated (Tab.7)
355 using the equation of $10^3 \ln \alpha_{\text{pectolite-water}} = 4.08 \cdot T^{-2} - 7.71 \cdot T^{-1} + 2.28$ proposed by Zheng (1993).
356 All three pectolite species are devoid of any fluid inclusions, so it was impossible to obtain
357 the formation temperature of larimar directly from the homogenization temperatures of its
358 inclusions. Hence, the average temperature (i.e. 139 °C) obtained from various empirical
359 chlorite geothermometers (see Tab. 5) was adopted to calculate the $\delta^{18}\text{O}$ compositions of
360 larimar-forming fluids, which fall within the range of -1.23 to 2.02‰, -0.96 to 3.02‰, and -
361 1.61 to 7.31‰ for Pct-I, Pct-II, and Pct-III, respectively (see Tab.7). Meanwhile, the
362 measurements conducted on two samples of host basaltic rocks yielded $\delta^{18}\text{O}$ values from
363 +2.84 to +4.33‰.

364 The δD values for all colour types of the pectolite are anomalously low and cover the
365 overall range between -390.51 and -294.02‰. The lowest δD values, with a mean of -
366 361.53‰, have been encountered in blue pectolite (Pct-II). The mean values for green (Pct-I)
367 and white pectolite (Pct-III) are slightly lower (i.e. -316.95‰ and -341.22‰, respectively).
368 Finally, there is also no correlation between δD and $\delta^{18}\text{O}$ values in the investigated pectolite

369 samples (i.e. $R^2 < 0.1$). Regarding host basaltic rocks, δD values are relatively high and fall
370 between -102.72 and -96.31% .

371

372 **5. Discussion**

373 5.1. Constraints on the origin of pectolite-forming fluids

374 Three distinctive aspects related to the formation of gem-quality pectolite from the
375 Dominican Republic (i.e. larimar) were discussed: (1) the temperature of mineralizing fluids,
376 and (2) their nature (magmatic versus meteoric), as well as (3) the fluctuations of
377 physicochemical conditions during the transition from green, via blue, towards white types of
378 pectolite, all found within single gem-quality larimar bodies.

379 The temperature (1) of pectolite-forming fluids cannot be directly estimated since the
380 samples lack any fluid inclusions that would be used to measure the appropriate
381 homogenization temperatures in Pct-I-III types. Based on the results obtained from chlorite
382 thermometry, it may be still assumed that crystallization of the pectolite occurred in relatively
383 low-temperature conditions, i.e. below ca. $170\text{ }^\circ\text{C}$ (see **Tab. 5**). The formation of Mg-chlorites
384 at the expense of primary clinopyroxene, along with ubiquitous pectolitization, could be at
385 least partially regarded as contemporaneous processes as intergrowths of pectolite and clay-
386 group species have been observed in association with the pyroxene relicts (**Fig. 7d**).

387 Regarding the nature of the mineralizing fluids (2), the oxygen isotopic data for
388 various pectolite types (**Tab. 7**) can be quite supportive. The values obtained in the following
389 study, though variable and ranging between $6\text{-}15\text{ }‰$, are fairly similar to those recorded for
390 pectolite species coming from different localizations around the globe. For instance, Wenner
391 et al. (1979) reported $\delta^{18}\text{O}$ values between $8.9\text{-}12.4\text{ }‰$ for rodingite-hosted pectolite from
392 western USA, whilst Craw et al. (1995) obtained δO values between $7.5\text{-}10.5\text{ }‰$ for pectolite

393 found in debris flow from Southland in New Zealand. In both cases, they concluded that
394 mineral must have formed via crystallization from low-temperature fluids, such as meteoric
395 waters (Craw et al., 1995; Wenner, 1979). The range of $\delta^{18}\text{O}$ values that were calculated for
396 blue and green pectolite-forming fluids in the Dominican Republic fall close to oceanic
397 waters. Meanwhile, they are slightly higher than present-day or ancient meteoric waters
398 reported in the vicinity of the study area, but also lower than values typical for volcanic and
399 magmatic waters (Fig. 13). The $\delta^{18}\text{O}$ values calculated for white pectolite-forming fluids
400 reveal the bimodal distribution and lay either close to oceanic or magmatic/volcanic waters
401 (Fig. 13). The $\delta^{18}\text{O}$ values of the host (altered) basaltic rocks are also indicative of the influx
402 of meteoric waters. This stems from the fact that the obtained values (i.e. 2.8-4.3 ‰; Tab.) are
403 low relative to MORB and OIB basalt that show relatively restricted ranges of $\delta^{18}\text{O}$ values,
404 i.e. 5.7 ‰ and between 4-6‰, respectively (Bindeman et al., 2020). According to e.g. Taylor
405 (1971), Feeley et al. (2008), and Bindeman (2020), the shift towards high $\delta^{18}\text{O}$ values in
406 basaltic rocks can be attributed to low-temperature fluid-rock interactions, whereas low $\delta^{18}\text{O}$
407 values (i.e. below ca. 5 ‰) suggest the influence of high-temperature alteration and/or the
408 influx of heated meteoric waters.

409 Meanwhile, the remarkable isotopic variations between green, blue, and white
410 pectolite species (Pct-I-III) can be explained by the precipitation in a boiling-related
411 environment and the corresponding removal of the vapor phase (Li et al., 2021). According to
412 Harris (1989), who investigated oxygen isotope zonation within single agate nodules, the
413 crystallization from H_2O vapor or H_2O liquid can thus result in relatively low and high $\delta^{18}\text{O}$
414 values in alternating chalcedony layers of agate, respectively. The effects of exchange
415 between fluids and rock-forming minerals (e.g. pyroxene) during secondary alterations (e.g.
416 chloritization) could also result in high $\delta^{18}\text{O}$ values of large, fan-shaped crystals of Pct-III.
417 This conclusion can be partially supported by low $\delta^{18}\text{O}$ values of altered basaltic rocks. Once

418 the alternating fluids (high-temperature magmatic waters and/or meteoric waters) interacted
419 with magmatic phases and resulted in low observed $\delta^{18}\text{O}$ values for basaltic rocks (i.e. 2.8-4.3
420 ‰), the output fluids (i.e. postdating pyroxene alteration) must have been itself enriched in
421 heavy O isotope, assuming that water/rock ratios were low (Harris, 1989). These ^{18}O -enriched
422 fluids could be further involved in the formation of white, fan-shaped crystals of pectolite
423 (Pct-III). On the contrary, one should bear in mind that the crystallization temperatures of
424 particular color pectolite types have not been necessarily the same during the formation of
425 single larimar bodies. Thus, the temperature drop could be another possible mechanism
426 responsible for the increase in $\delta^{18}\text{O}$ values reported for Pct-III. Hereafter, assuming the
427 isotopic composition for the invading fluids was constant, the formation temperature of white
428 pectolite (Pct-III) must have been up to ca. 70 °C lower than in green species (Pct-I). This
429 scenario is plausible as Pct-III fibers reveal slightly different morphology (i.e. larger and
430 loosely bound fibers) than Pct-I and II (see Fig. 4b, d, f). Hence, the possible crystallization
431 sequence of larimar bodies involved green (Pct-I) → blue (Pct-II) → white species (Pct-III).

432 Finally, the changes in physicochemical conditions during pectolitization can be
433 further resolved based on combined CL and EMPA analyses. Particularly, the transition from
434 Pct-I, towards Pct-II, to Pct-III could be accompanied by the shift from oxic towards a more
435 reducing (suboxic) environment. This stems from the fact that Pct-I is poor in Mn, which may
436 be related to low $\text{Mn}^{2+}/\text{Mn}^{3+}$ ratios in mineral-forming fluids, although quenching of
437 luminescence by the addition of Fe could also affect CL properties of the mineral. Instead, an
438 intense yellow CL of Pct-II and Pct-III could be linked to the presence of $\text{Mn}^{2+}\text{-Ca}^{2+}$
439 substitution, which requires high $\text{Mn}^{2+}/\text{Mn}^{3+}$ ratios in invading fluids (and corresponding
440 suboxic crystallization conditions). Similar considerations regarding the nature of
441 mineralizing fluids have been widely reported in studies focused on carbonate diagenesis
442 (chiefly calcite), where CL properties of calcite (and the corresponding presence of Mn at the

443 divalent or trivalent oxidation stage) can be used to reconstruct changes in redox conditions
444 during the formation carbonate deposits through geological time (Beaudoin et al., 2011; Wang
445 et al., 2017). The proposed scenario can be additionally supported by the presence of iron
446 oxides and zeolites (natrolite) in association with Pct-I, followed by the abundance of native
447 copper and copper sulfides in Pct-II (blue).

448 Another issue is that the larimar bodies not only comprise alternating green, blue, and
449 white, pectolite-rich bands but may also show a characteristic polygonal appearance (i.e.
450 isometric rectangular and oval-shaped areas made of blue or green pectolite crosscut by veins
451 of white-colored variety) - see Fig. 3. Radial growth of green pectolite Pct-I (Fig. 4b) suggests
452 crystallization in open spaces within the host volcanics (Albers et al., 2019), whilst the
453 abundance of concentric arrangement of green, blue and white pectolite (Fig. 3) invokes that
454 the mechanisms of larimar formation could be similar to those reported for agate nodules, i.e.
455 involved post-magmatic hydrothermal-fluid flow of variable physicochemical properties. The
456 polygonal variety of larimar, in turn, can be triggered by tectonic movements, which started in
457 Lower-Middle Pliocene and continued to the present, such as duplex deformations that were
458 noted for larimar host basaltic rocks (Espí and Obieta, 2017). Similar patterns (referred to as
459 „raindrops”) have also been reported in natural turquoise where its origin is related to the
460 pseudomorphic replacement of pristine phosphates such as apatite (Liu et al., 2020). It might
461 be thus speculated that the polygonal appearance in some larimar specimens may result from
462 two-stage pectolitization, i.e. the formation of blue or green pectolite after resorbed mafic
463 phases (pyroxene, olivine; see Fig. 7d), followed by the crystallization of another pectolite
464 generation (white) in fissures, vugs, and/or within the groundmass of volcanic rocks.
465 However, further detailed studies are required to confirm this scenario.

466 According to Brandt et al. (1987), Wenner (1979), and Kuroda et al., (1979), δD
467 values of pectolite are extremely low (i.e. even below -400‰) and cannot be explained by

468 temperature variations and/or Reyleigh fractionation effects. Otherwise, such low values can
469 be explained by the size of the O-H-O bridges in the mineral structure, resulting in the
470 preferential incorporation of a light hydrogen isotope instead of a heavy one (Brandt et al.,
471 1987). Thus, D/H isotopic fractionation factors for pectolite can be extremely low (e.g. around
472 0.6; see Wenner (1979). Brandt et al. (1987) have concluded that δD values for pectolite
473 cannot be used while determining the hydrogen isotopic composition of mineral-forming fluid
474 (i.e. δD values of input fluids do not affect δD values of pectolite). The δD values for all
475 investigated pectolite types (Pct-I-III) are consistent with those observations as they roughly
476 fall below -300 ‰ (Tab. 7). However, their contribution to the knowledge of the character of
477 larimar-forming fluids remains insignificant though.

478

479 5.2. Potential sources for pectolite-forming elements

480 Overall, pectolite-forming elements (chiefly Ca, Na, and Si) can be derived from either
481 external (e.g. country rocks, seawater) or internal (e.g. magmatic-related residual fluids)
482 sources. The former scenario seems to be less probable, though there are some occurrences of
483 Early Pliocene evaporitic sediments in the close vicinity of the study area, i.e. within the
484 Enriquillo basin (Mann et al., 1999), that could act as a potential reservoir for both Na and Ca.
485 The additional source of Ca could be also limestones overlying the larimar host volcanic
486 rocks, but they are younger than larimar. Meanwhile, the Miocene-Pliocene tectonic changes
487 in the Hotte Selle Bahoruco region created the migration paths for Na- and Ca-bearing fluid
488 within the volcanic rocks. On the other hand, seawater as the potential reservoir for Na is also
489 probable due to the close vicinity of the Caribbean Sea. Moreover, the calculated isotopic
490 oxygen composition of pectolite mineralizing fluids falls in the range diagnostic of oceanic
491 waters (Fig. 13). However, Espi and Obieta (2017) based on microthermometric

492 measurements of inclusions found in calcite coexisting with pectolite found mineralizing fluid
493 had salinity in the range of 3.5-5.5 % eq. NaCl, which was somewhere above the salinity of
494 seawater, and more diagnostic of hydrothermal fluid or its mixture with seawater.

495 The second (i.e. auto-hydrothermal) scenario is, in turn, confirmed by the
496 mineralogical and microtextural studies of host basaltic rocks of the Dumisseau Formation in
497 the Sierra de Bahoruco region in the south-west part of the Dominican Republic. Firstly, these
498 rocks contain partially chloritized clinopyroxene, i.e. diopside with the average formula of
499 $(\text{Ca}_{0.85}\text{Na}_{0.15})(\text{Ti}_{0.11}\text{Fe}^{3+}_{0.06}\text{Mg}_{0.74}\text{Fe}^{2+}_{0.08})(\text{Si}_{1.87}\text{Al}_{0.05}\text{Fe}^{3+}_{0.08})\text{O}_6$ that could serve as a source
500 for Ca and Na (note these elements are not fixed with newly formed chlorite and can further
501 participate in fluid-rock interactions, i.e. pectolitization). The alterations of basaltic rocks
502 might have also resulted in the desilicification due to the formation of silica-poor phases such
503 as chlorite-group species at the expense of pyroxene and the corresponding increase of Si at
504 the post-magmatic stage (Powolny et al., 2019). Secondly, the occurrence of aegirine-augite
505 microlites within the groundmass of volcanic has been observed. Thus, the parental magma,
506 though tholeiitic (picritic) in nature (i.e. Mg and Fe rich, with olivine as the main phase), has
507 likely been affected by the increase of alkalis during the final stages of its evolution. The
508 enrichment in alkalis could be related to the presence of mantle plume and magma-
509 asthenosphere interactions that led to the formation of OIB-like geochemical fingerprints in
510 the investigated rocks. Na_2O along with other volatiles have likely been concentrated in late-
511 stage, residual magmatic fluids and were further involved in the formation of pectolite
512 (Caredda et al., 2003). Another possible source for Na and Ca is the garnetization of
513 plagioclases, which has been mostly reported in pyroclastic deposits containing larimar bodies
514 in the Sierra de Bahoruco region (Wachowiak et al., 2022). Finally, minor amounts of K and
515 Fe fixed with a green variety of pectolite (Pct-I) could be leached from groundmass minerals
516 (Weska et al., 2020).

517

518 5.3. Element mobility during pectolitization

519 According to Grant (1986, 2005) the mobility of main and trace elements during
520 pervasive alterations of igneous or sedimentary rocks (Kuwatani et al., 2020) or even during a
521 single hydrothermal-metasomatic process such as albitization (Kaur et al., 2012) can be
522 reconstructed based on so-called isocon diagram (*iso* - constant; *con* - concentration). This
523 type of plot shows the contents of the elements (in wt.% or ppm) in weakly-altered (or fresh)
524 rock samples and their strongly altered equivalents (or certain primary and secondary phases,
525 e.g. Na-Ca plagioclase and albite). As a result, the behaviour of these elements, i.e. gain or
526 loss during secondary alteration is revealed by the so-called isocon, which represents a
527 straight line defined by constant mass/volume changes and/or concentrations of immobile
528 species such as Al, HFSE, Zr, Y, etc. (Grant, 1986, 2005). Hence, to trace the geochemical
529 changes during the ubiquitous pectolitization, the composition of the larimar-rich rock against
530 its original, larimar-poor rock was demonstrated on the graph, called isocon diagram (Fig.
531 14).

532 Regarding the mobility of main elements, the formation of pectolite has resulted in
533 the remarkable increase of Na₂O, SiO₂, and P₂O₅ that fall above the isocon (Fig. 14a). This
534 behaviour simply stems from the relatively high contents of Na and Si in pectolite, whereas
535 mobilization of P could be explained by the fact that the formation of pectolite has partially
536 involved alteration of tree trunks captured by magma flow, though enhanced crystallization of
537 apatite-group minerals cannot be excluded as well at this stage of rock evolution. Moreover,
538 according to Liu et al. (2020), phosphorus can be mobilized via interaction between rock and
539 meteoric waters. HREE and HFSE elements (e.g. Nb, Ta, Th, Zr) were not mobilized during
540 ubiquitous pectolitization of host rocks as they almost lie on the straight line that defines the

541 slope of the isocon (Fig. 14b). LREE and Eu can also be considered immobile. Otherwise,
542 fluid mobile LILE elements including Cs, Rb, Ba, and Sr fall above the isocon and thus they
543 were gained during the pectolitization. These elements could be preferentially concentrated in
544 hydrothermal post-magmatic fluids, following syn- to post-volcanic alterations and/or
545 weathering of primary phases such as pyroxene or groundmass minerals. Sr, for instance,
546 could be leached from primary Ca-bearing phases and incorporated into pectolite via Ca^{2+} -
547 Mn^{2+} isovalent substitution. Rb and Cs, in turn, can reflect the contemporaneous formation of
548 hydrous K-bearing phases (e.g. clay-group species such as illite or mixed layer clays) where
549 K-Rb or K-Cs substitutions can occur. Similar elemental transfers (i.e. LILE enrichment)
550 changes have been reported by e.g. Powolny et al. (2018) during their studies on strongly-
551 altered trachyandesites that were affected by spilitization (Na-metasomatism that leads to the
552 formation of secondary albite accompanied by other low-temperature hydrous phases). During
553 pectolitization some increase of such transition metals as Ni, Co, Cr, and Sc was noted. These
554 elements could be also remobilized along with the alteration of early-stage magmatic phases
555 such as spinels found in the larimar host volcanic rocks and/or originated from external
556 sources, e.g. meteoric waters (Liu et al., 2020).

557 There is a clear link between the formation of larimar bodies and the abundance of
558 native copper (and minor Cu-sulfides) that represents another distinctive feature of the larimar
559 deposit in Sierra de Bahoruco. Although volcanic rocks from the study area do not contain
560 economically valuable Cu contents and are mined mostly due to the larimar occurrences, it
561 should be mentioned that the Dominican Republic is famous for Au–Ag–Cu deposits found in
562 Sánchez Ramírez Province, in the central part of the country (Nelson et al., 2023). These
563 deposits can be described as an epithermal VMS type related to volcanic activity during early-

564 Cretaceous extension and subsequent interactions between rock and seawater (Nelson et al.,
565 2023).

566 In general, several geological processes may lead to the precipitation of epigenetic
567 native copper among volcanic and sedimentary environments, though early magmatic origin
568 has also been postulated. These processes occur under a relatively wide range of temperatures
569 and involve several mechanism, such as: the reduction of Cu-sulfides, crystallization from Cl-
570 bearing solutions, organic activity, and/or mixing between volcanic-related and groundwater
571 solutions, etc. (Baggio et al., 2018; Bing-Quan et al., 2007; Bodden, 2019; Cornwall, 1956).
572 As referenced to the presence of native copper at the boundary between green and blue
573 pectolite, it was likely promoted by the latter (fluid mixing) mechanism (Bodden, 2019; Pinto
574 et al., 2011), but the transition from oxic to suboxic environment (see previous subchapters)
575 and/or fluid boiling (Li et al., 2021; Schaarschmidt et al., 2021) could also be of vital
576 importance. Another crucial factor was likely the devolatilization and escape of sulphur
577 (Radhakrishna and Pandit, 1972) during the initial stages of Cretaceous volcanism in the
578 study area. Thus, native copper, instead of e.g. copper sulfides, has emerged. The source of
579 Cu could be again primary and heavily altered magmatic phases (pyroxene, olivine), but also
580 opaques (e.g. spinels) - see Baggio et al. (2018) and Pinto et al. (2011). Alternatively,
581 limestones found in the upper parts of the profile (see Fig. 1) could eventually serve as a
582 reservoir for Cu-bearing fluids (Francis, 1972).

583 **6. Conclusions**

584 (1) Gem-quality larimar bodies hosted by basaltic rocks of Dumisseau formation involve
585 green (weak to brownish luminescent; containing traces of K and Fe), blue (yellow
586 luminescent, Mn-rich, and associated with copper sulfides), and white (also yellow

587 luminescent and Mn-rich) varieties of pectolite. Their formation occurred in a relatively low-
588 temperature range, as supported by the crystallization temperatures of coexisting Mg-chlorite
589 (i.e. below 170 °C) and was likely maintained by the infiltration of volcanic-related deuteritic
590 fluids mixed with meteoric waters. Possible changes in physicochemical conditions (i.e.
591 oxic→suboxic) during the progressive pectolitization and devolatilization favored the co-
592 precipitation of native copper along with the formation of blue pectolite.

593 (2) Following oxygen isotope variations, the transition starting from green ($\delta^{18}\text{O}$ of +6.38 -
594 +9.66‰), via blue ($\delta^{18}\text{O}$ of +8.59 - +10.67‰), and ending with white ($\delta^{18}\text{O}$ up to 14.99‰)
595 can be ascribed to the temperature decrease during the influx of hydrothermal fluids and/or
596 boiling-related conditions (i.e. crystallization from water vapor in the case of green and blue
597 pectolite or water liquid in the case of white pectolite).

598 (3) Na and Ca, representing the main mineral-forming elements of pectolite, have been at
599 least partially derived from deuteritic solutions exsolved from host basaltic melts of OIB-
600 related affinity but could be also leached due to the breakdown of pristine Na- Ca bearing
601 phases such as pyroxene (i.e. aegirine-augite, diopside). The latter frequently occur as
602 partially chloritized phenocrysts and microlites disseminated in the groundmass of host
603 volcanic rocks, suggesting the increase of alkalis (Na+K) during the final stages of magma
604 solidification.

605 (4) Pectolitization has resulted in the mobilization of LILE elements such as Sr, Cs, Ba, and
606 Rb that could be incorporated by both pectolite and associate phases (zeolite, clay group
607 species). Transition metals including Cu, Cr, Co, Cu, and Ni have also been introduced along
608 with pectolite-forming fluids. These elements were derived from the alteration of early-stage
609 magmatic phases (e.g. Fe and Cr-bearing spinel).

610

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615

616 **Data Availability**

617 All data generated or analyzed during this study are included in this published article.
618 Correspondence and requests for materials should be addressed to M.D.-S.

619

620 **Competing interests**

621 The authors declare none.

622

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856 **Figures and Tables**

857 **Fig. 1** (a) Position of larimar mine within Hispaniola Island; (b) Main lithologies found in the
858 vicinity of the Las Filipinas larimar mine; (c) Cross-section along SW-NE showing the spatial
859 relationship between larimar-bearing basaltic rocks and adjacent sedimentary rocks

860 **Fig. 2** (a) Field exposure showing the contact between larimar-bearing volcanic rocks (i.e.
861 basalts and pyroclastic deposits) and overlying sedimentary deposits (limestones). (b)
862 Schematic sketch of main lithologies exposed in the study area (Meznaric et al., 2018),
863 modified based on own observations

864 **Fig. 3** Examples of gem-quality larimar samples comprising green (Pct-I), blue (Pct-II), and
865 white (Pct-III) variety of pectolite surrounded by host basaltic rocks. Note the presence of a
866 polygonal variety (upper left), as well as the gradual transition between species in a single
867 larimar body (upper right and lower right). The presence of an iron oxide-rich layer at the
868 basalt-larimar contact is, in turn, visible in the sample from the lower left part of the image

869 **Fig. 4** Photomicrographs (a, c, e) and the corresponding BSE images (b, d, f) of particular
870 pectolite types. (a) Radiating (fan-shaped) crystals of Pct-I at the boundary with host basaltic
871 rock. Note the presence of elongated natrolite (Ntr); (b) The BSE image of Pct-I; (c) Tightly
872 interlocked crystals of Pct-II at the boundary with Pct-I; (d) The BSE image of Pct-II; (e)
873 Massive Pct-III filling the inner region of larimar body; (f) The BSE image of Pct-III. Note

874 that all BSE images were acquired under the same magnification to underline the differences
875 in the size of particular fibers

876 **Fig. 5** (a) Accumulation of native copper (nat-Cu) at the boundary between Pct-I (green) and
877 Pct-II (blue) and (b) Copper sulfides (chalcocite) distributed within Pct-II (blue)

878 **Fig. 6** (a, b) Cathodoluminescence (OM-CL) images showing the transition between Pct-I,
879 Pct-II, and Pct-III, along with corresponding changes in cathodoluminescence colors (i.e.
880 from weak brown to bright yellow). CL spectra of particular species, in the range of 200-900
881 nm, have been shown at the bottom part of the figure. Note that Mn²⁺I (564, 570 nm) and
882 Mn²⁺II (577, 585 nm) refer to Mn impurities found in two various structural positions, where
883 they substitute for Ca²⁺

884 **Fig. 7** Photomicrographs of larimar host basaltic rocks: (a) Altered (i.e. chloritized; Chl)
885 phenocrysts of pristine pyroxene and/or olivine surrounded by iddingsite-rich (Idn) layer.
886 Note the presence of microcrystalline volcanic glass comprising pyroxene microlites (Px)
887 with second-order interference colors; (b) Serpenititized (Srp) olivine surrounded by
888 pyroxene (Px) - the latter is partially transformed into chlorite (Chl). Note the presence of
889 spinel-group species (magnetite; Mag); (c) Fe-Cr-bearing spinel (magnetite-chromite series;
890 Fe-Cr Spl) surrounded by iron oxides (Fe-ox), followed by volcanic groundmass where
891 subhedral pyroxene microlites (Px) and clay-group species (Clay-g) can be distinguished; (d)
892 Pectolite in association with clay-group species, both filling the area that has been formerly
893 occupied by pyroxene (Px)

894 **Fig. 8** The composition of phenocrystic pyroxene (red cross) and microlites (black cross)
895 plotted on the Quad-Jd-Aeg diagram (Morimoto et al., 1988). Note relict of pyroxenes found
896 in the phenocrysts represent Ca-Mg-Fe species, while microlites are Ca-Na species

897 **Fig. 9** The composition of phenocrystic pyroxene plotted on a Wo–En–Fs triangular diagram
898 (Morimoto et al., 1988)

899 **Fig. 10** The composition of replacive chlorite plotted on Al +Vac–Mg–Fe compositional
900 classification diagram (Zane and Weiss, 1998)

901 **Fig. 11** Chemical composition of the investigated Mg-chlorite plotted on T–R²⁺–Si plot
902 (Bourdelle and Cathelineau, 2015), where R²⁺ corresponds to the sum of divalent cations

903 **Fig. 12** Histograms of distribution of $\delta^{18}\text{O}$ (A) and δD (B) values among particular pectolite
904 types (Pct-I-III)

905
906 **Fig. 13** Histogram showing oxygen isotope compositions of the pectolite-forming fluids
907 calculated according to the equation of Zheng (1993): $10^3 \ln \alpha_{\text{pectolite-water}} = 4.08 \cdot T^{-2} -$
908 $7.71 \cdot T^{-1} + 2.28$. The formation temperature of 139 °C (average based on chlorite thermometry
909 that utilizes Al^{IV} contents and combined Al^{IV} contents and Fe/Fe+Mg) has been assumed.
910 Note that the range of $\delta^{18}\text{O}$ for meteoric waters in the vicinity of the study area (Gourcy et al.,
911 2022; Holmes et al., 2023; Suarez et al., 2010), oceanic waters and volcanic waters, as well as
912 metamorphic, ultramafic, and basaltic rocks (Grossman, 1998; Hoefs, 2009; Sharp, 2017)
913 were added for comparison. Note the bimodal distribution of $\delta^{18}\text{O}_{\text{fluid}}$ for Pct-III (white) that
914 argues for temperature decrease or effects of fluid boiling

915
916 **Fig. 14** Isocon diagram showing gain and loss of main (a) and trace (b) elements during
917 incipient pectolitization of host basaltic rocks. Note that the content of Al₂O₃ and
918 $\Sigma(\text{HREE}+\text{Th}+\text{Nb}+\text{Ta}+\text{Y}+\text{Zr})$ was used *a priori* to create the isocon for main and trace
919 elements, respectively. According to e.g. Winchester and Floyd (1977) and MacLean and
920 Barrett (1993) these elements are considered immobile during fluid-rock interactions. Scaling

921 factors have been added to provide a user-friendly data visualization (i.e. gain and loss of
922 particular elements)

923

924 **Tab. 1** The operating conditions of EMPA analyses of pectolite, pyroxene, and chlorite

925 **Tab.2** Representative composition (EMPA) of three color types of pectolite species

926 **Tab. 3** Representative clinopyroxene composition (EMPA) found in basaltic rocks. Note:

927 $\#Mg = Mg^{2+}/(Mg^{2+}+Fe^{2+})$; Fe^{2+} and Fe^{3+} calculated from the charge balance; $J=2Na$; $Q =$

928 $Ca+Mg+Fe^{2+}$

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930 **Tab.4** Representative composition (EMPA) of replacive chlorite (after diopside). Note: R^{2+} is

931 the sum of divalent cations ($Fe+Mg+Mn$) assuming all iron to be ferric (Fe^{2+}); $Mg\#$ is

932 $Mg/(Mg+Fe)$

933

934 **Tab. 5** Summary of crystallization temperatures for Mg-chlorite based on empirical and semi-

935 empirical geothermometers

936 **Tab.6** Whole-rock major and trace composition for larimar-rich and larimar-poor volcanic

937 rocks. Note: L.O.I. - loss on ignition; $Mg\#$ - molar $MgO/(MgO + FeO)$; $Eu^* = (Sm_{CN} \cdot Gd_{CN})^{1/2}$;

938 $_{CN}$ - chondrite-normalized; $A/CNK =$ molar $[Al_2O_3/(CaO+Na_2O+K_2O)]$; $A/NK =$ molar

939 $[Al_2O_3/(Na_2O+K_2O)]$; LREE: La-Sm; HREE: Gd-Lu

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941 **Tab.7** $\delta^{18}O$ and δD values for particular color types of pectolite Pct-I-III. Note that two

942 measurements for the host rock have also been included (HR-01-02)

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