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3 **THE “LOESS” DEPOSITS OF BUCA DEI CORVI SECTION (CENTRAL ITALY)**
4 **REVISITED**
5

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20

21 **Abstract**
22

23 Loess deposits have been described in the past for the upper section of Buca Dei Corvi succession
24 (Central Italy). In this paper the deposits were re-analyzed to clarify the depositional environment
25 and to attempt a paleoclimate reconstruction. Two radiocarbon dates on pedogenic carbonate
26 constrain the ages to the Late Glacial, and are consistent with previous OSL dating of the top of the
27 succession. The non-marine mollusc assemblage shows typical character of cold and dry climatic
28 conditions, testified by strong oligotypical composition. Mineralogy and geochemistry of the
29 sediments indicate the abundant presence of exotic quartz mineral which can be explained only by
30 wind transport. Probably, wind transport was also responsible of deposition of carbonate which then
31 dissolved and re-precipitated producing pedogenic concretions. Stable isotopes (¹³C/¹²C and ¹⁸O/¹⁶O
32 ratios) of the concretions are consistent with a climate drier than present conditions, with an
33 environment characterized by sparse vegetation.
34

35 **Keywords:** non-marine molluscs, pedogenic carbonate, stable isotopes, Late Glacial, Italy
36

37

38 **1.Introduction**

39 In the review of loess deposits throughout Italy, Cremaschi (1990) did not report any finding south-
40 west of the Apennine chain. More recently, the possibility of the occurrence of phases of aeolian
41 dust aggradation during cold periods in more southerly positions than previously reported has been
42 re-assessed (e.g. Giraudi et al., 2013). Specifically for Tuscany, Sarti et al. (2005), reported
43 evidence of loess deposition within the succession cropping out at the Gulf of Baratti (Fig. 1). In
44 this paper we discuss the presence of loess deposits in the Buca dei Corvi section (Fig. 1), one of
45 the most important Late Quaternary sections of the Tyrrhenian coast of Central Italy, and report
46 new stratigraphic, chronological, paleontological and geochemical data. The “Buca dei Corvi”
47 section (literally “the Hole of the Ravens” 43°24’47” N 10°24’12”) is one of the best studied and
48 most completely exposed Late Quaternary geological successions on the Tyrrhenian coast north of
49 Rome, and contains a discontinuous record of the Upper Pleistocene sea level oscillations. In
50 particular, the basal level is a rich marine fossil-bearing site, containing the so-called “warm guests”
51 mollusc (Blanc, 1953, Ottman, 1954; Nisi et al., 2003), and it was one of the sections anchored with
52 aminostratigraphy in the classic work of Hearty et al. (1986) on the Mediterranean raised beaches.
53 On the basis of this work the basal fossiliferous coastal deposit was correlated with the Marine
54 Isotope Stage 5e (MIS5e). Subsequently, Mauz (1999) obtained new age measurements, using the
55 optically stimulated luminescence technique (OSL), for the basal layer (>108 ka) then 94 ± 34 at
56 intermediate depth, and finally $9.7\pm$ ka for the upper part of the section. As a result, the Buca dei
57 Corvi is one of the few relatively well-dated coastal successions of Late Quaternary of the
58 Tyrrhenian coast of Italy (e.g. Hearty et al., 1986, Mauz, 1999). Interestingly Ottman (1954)
59 reported the presence of fine-grained “loess” deposits in the top part of the succession in the road
60 cut of the Via Aurelia close to Castiglioncello village (Fig. 1). The presence of these deposits was
61 not further investigated and they represent the target of this contribution.

62

63 **2.Geological and morphological setting**

64

65 The coastal area can be grossly divided in two main morphological units corresponding to Terrazzo
66 I and Terrazzo II of Federici and Mazzanti (1995). The “Terrazzo I” corresponds to a polycyclic
67 marine-continental terrace with the base related to marine transgression culminating in the high
68 stand of MIS5e (Federici and Mazzanti, 1995; Zanchetta et al., 2006). The “Terrazzo II”, which
69 locally is uplifted to ca. 125 m a.s.l., is again a polycyclic terrace, probably originating at the MIS11

70 (Zanchetta et al., 2006). The Buca dei Corvi section is located at a narrow coastal inlet at the
71 northern sector of the “Terrazzo I”, developed in a paleovalley (Ciulli, 2005, Fig. 1).

72 The local substrate of the Buca dei Corvi section consists of Upper Jurassic serpentinite (Bartoletti
73 et al., 1985). According to the revised stratigraphy proposed by Ciulli (2005) and shortly presented
74 in this work, the Late Quaternary section can be divided into 11 different lithostratigraphic units
75 (LU) (Fig. 2), which are, from the base to the top:

76
77 LU1 (10-11.80 m) – Deposit composed by layers of grey and light brown coarse-grained sand, and
78 very coarse-grained sands with marine mollusc shells and well-rounded pebbles. In this unit, Blanc
79 (1953) and more recently Nisi et al. (2003) found fossil remains of warm molluscan faunas.
80 According to Hearty et al. (1986) LU1 belongs to aminozone E, correlated with MIS5e.
81 Consistently, Mauz’s (1999) OSL data yielded an age >108 ka.

82
83 LU2 (11.80-12.10 m) – It is composed by very red massive-silty sand, with the base containing
84 strongly altered bioclasts and litharenite fragments from LU1. It can be interpreted as a well
85 developed paleosol (Zembo et al., in progress).

86
87 LU3 (12.10-15.50 m) – Fine-yellow and light-brown cemented sand, with tangential cross
88 stratification and convolute bedding and a pin-stripe lamination with foraminifer fragments
89 (aeolian).

90
91 LU4 (15.50-20.60 m) – Cemented sands characterized by low-angle cross and concave
92 stratifications, with rounded pebbles and marine mollusc fragments. At the top of this unit there are
93 evident carbonate concretions indicating sub-aerial exposure. The LU4 and LU3 have been dated by
94 Mauz (1999) at 94 ± 34 ka, which still indicates the late MIS5.

95
96 LU5 (20.60-22.00 m) – Massive red silty sands with dispersed pebbles (palaeosol).

97
98 LU6 (22.00-22.50 m) – Cemented sand level with subvertical carbonate concretions (aeolian
99 deposits?).

100
101 LU7 (22.50-25.00 m) – Clast-supported breccia with ophiolite clasts, faint stratification and fine-
102 grained matrix.

103

104 LU8 (25.00-29.00 m) – A yellow-orange massive fine-silty to fine-sand deposit with small
105 carbonate concretions and non-marine molluscs. The LU8 corresponds to the “loess” unit of
106 Ottman’s (1954) stratigraphy.

107

108 LU9 (29.00-29.50 m) – At the top of LU8 there is a darker brown massive silty-sand with non-
109 marine molluscs and rare small rounded clasts.

110

111 LU10 (29.50-32.90 m) – Deposit with low-angle planar cross and concave stratification, formed by
112 red silty-sand fining upward layers to very thick sandy layers, with oriented and concentrated
113 pebbles at the base. The origin of this layer is not very clear. According to Ottman (1954) this
114 represents reworking of loess. Mauz (1999) dated LU10 sediments with OSL at 9.7 ± 2.4 ka and
115 interpreted them as backshore deposits.

116

117 LU11 (32.90-33.70 m) – Present soil.

118

119 Overall, this stratigraphic reconstruction is generally consistent with that proposed by Ottman,
120 (1954) and with the less detailed stratigraphy proposed by Mauz (1999). Fig. 2 shows the general
121 stratigraphy with the OSL dates of Mauz (1999). The subjects of our discussion are LU9 and LU8.

122

123 **3. Material and methods**

124

125 Different levels were sampled over the LU8 and LU9 for lithological, geochemical, isotopic,
126 paleontological and pedological investigations (Figs. 3, 4). Before sampling the surface was
127 excavated for some tens of centimetres to reach the fresh deposit.

128

129 *3.1 Sedimentological and geochemical analyses*

130

131 Samples were collected discontinuously starting from ca. 25 m a.s.l., close to the base of the LU8,
132 up to the very top of LU9 (Fig. 3). Subsamples of ca 0.5 kg were dried in an oven at 105 °C for 24
133 hours and then powdered. The powders were analysed using X-ray diffraction (XRD) for
134 determining the main mineralogical phases, and with the XRF method for major oxide composition
135 and trace element contents. The carbonate content of the samples was determined through
136 gasometry (with calibration to pure calcite) as described by Leone et al. (1988). Replicate analyses
137 show a mean reproducibility ca. $\pm 5\%$ (usually over a set of three replications). Part of the remaining

138 samples were sieved mechanically and fractions of >1 mm and >0.5 mm were inspected under a
139 binocular microscope. From these fractions carbonate concretions were selected. Carbonate
140 concretions were cleaned in an ultrasonic bath using deionized water, dried, powdered, checked for
141 mineralogical composition using XRD, and then analysed for oxygen and carbon stable isotopes.
142 The samples were analysed at SUERC (East Kilbride, Scotland) with an AP2003 mass spectrometer
143 equipped with a separate acid injector system, after reaction with 105% H₃PO₄ under He
144 atmosphere at 70 °C. The isotopic results are reported using the conventional δ‰-notation, relative
145 to V-PDB; δ¹⁸O values of water are quoted relative to V-SMOW. Mean analytical reproducibility
146 (±1σ) was ±0.08‰ and ±0.10‰ for carbon and oxygen, respectively. During the period of analyses,
147 samples of internal laboratory standard (Carrara Marble) calibrated against NBS19 yielded a
148 reproducibility (±1σ) of ±0.07‰ and ±0.08‰ for carbon and oxygen respectively. For each level
149 three different concretions were analysed. Several modern pedogenic concretions were collected in
150 the area and analysed for comparison with old carbonate concretions isotopic data. They consist of
151 cylindrical carbonate concretion formed around roots (living and/or decaying, in the latter case roots
152 were still recognisable and related to present soil). According to Klappa (1980), they can be called
153 rhizoconcretions (Fig. 4B). Table 1 shows all the results for LU8-9, and Table 2 for the modern
154 pedogenic carbonates.

155 The entire succession is virtually devoid of significant organic matter remains and attempts for
156 dating were focused on carbonate concretions. Concretions from two different layers were analysed
157 by AMS ¹⁴C dating technique at Beta Analytic (Florida USA, Table 3). Samples were previously
158 washed in a mixture of deionized water and H₂O₂ and then etched with diluted HCl for a few
159 seconds, to eliminate possible superficial carbonate contamination. Calibration was performed using
160 the INTCAL13 database (Reimer et al., 2013). Ages obtained on this kind of material may have
161 some limitation because of possible contamination by old carbonates (difficult to detect even after
162 careful selection), because of possible hard-water effects, and because of possible processes of
163 dissolution/re-precipitation of CaCO₃ (Budd et al., 2002). Moreover, carbonate concretions in loess
164 are not necessarily synchronous with loess deposition, then representing a minimum age of the
165 deposits (Gocke et al., 2011).

166

167 *3.2 Paleontological analyses*

168 Two samples of ca. 5 kg were selected for the fossil study in LU8 and LU9 respectively. They were
169 dried in an oven for 2 days at 40 °C, then the sediment was disaggregated using a very dilute
170 solution of H₂O₂ and deionised water (ca. 5%). The material was then sieved using 2000, 1000, 500
171 and 250 μm mesh screens. All the identifiable shells and fragments were picked out under a

172 binocular microscope and counted using the convention of Sparks (1961) where every gastropod
173 apex is recorded to give a minimum number of individuals present. As adopted in the earliest
174 studies on the assemblages of terrestrial fossil mollusc of the Italian peninsula (e.g. Esu, 1981;
175 Crispino and Esu, 1995; Di Vito et al., 1998; Zanchetta et al., 2004, 2006; Esu and Gianolla 2009),
176 taxa were subdivided into ecological groups according to the scheme proposed by Ložek (1964;
177 1986; 1990; 2001).

178

179 *3.3 Paleopedological analyses*

180 The weathering profile was described in the field following Sanesi (1977) and sampled for bulk and
181 micromorphological analyses. The horizon nomenclature follows the terminology of the
182 internationally accepted guidelines proposed by FAO (2006). A Munsell Soil Color Chart was used
183 to determine soil colour on dry samples. For the micromorphological study, an undisturbed oriented
184 block was collected in the LU9 with Kubiëna box (Fig. 3). The thin section was prepared by the
185 *Laboratorio per la Geologia–Piombino* (Livorno, Italy) following the procedure of Murphy (1986).
186 The thin section, 120x90 mm, was observed with a polarizing transmitted light microscope under
187 plane (PPL) and cross polarized light (XPL) and described according Bullock et al. (1985) and
188 Stoops (2003, 2007); moreover, some concepts of Brewer (1964) were also taken into account and
189 the interpretation of micromorphological features was carried out following Stoops et al. (2010).
190 The origin and palaeoenvironmental significance of the weathering profile is mainly based on
191 micromorphological observations.

192

193 **4.Results**

194

195 *4.1 Field and pedological observations*

196 The outcrop section here described, about 9 m thick, is representative of the topmost units (from
197 LU8 to LU11, the present soil) of the Buca dei Corvi cliff–section, and was described along the
198 S.S.1-Aurelia starting from at an elevation of about 25 m a.s.l. (Fig. 2,3). LU10 is ca. 250 cm of
199 coastal eolianite to colluvial deposits on top weathered by a recent soil cover (LU11; Fig. 3 A,B).
200 The LU10 deposits are constituted by planar and trough cross–laminated sands, with alternating fine
201 and coarse laminae; subangular fine pebbles are locally concentrated at the base of the laminae,
202 often showing an erosive basal surface. LU10 is separated from LU9 by a clear erosional surface.
203 The LU9 is essentially sandy loam in texture, and consists of a massive and bioturbated calcic
204 horizon Bk, about 60 cm thick, marked by dull yellowish brown to yellow orange matrix colours
205 (Munsell color: 10YR 5/4–6/4; Fig. 3a), and a high frequency of coarsely-cemented pedogenic

206 concretions (Munsell color: 2.5Y 7/4). Carbonate concentrations (millimetres in size) are dispersed
207 throughout the matrix. This horizon is characterised by moderately developed prismatic to sub-
208 angular blocky structure with hard rupture resistance. The coarse ($\phi_{\max}= 5$ mm) and angular rock
209 fragments that do occur in this horizon are serpentinite clasts. Rare non-marine molluscs are also
210 preserved. As reported above, the upper limit of the Bk horizon is abrupt and indicates an erosional
211 surface truncating the topsoil horizons. The transition between the Bk horizon and the lower and
212 thicker (350 cm) LU8 is clear. The features of LU8 are broadly similar to those of LU9 except for
213 the pale-yellow matrix colour (Munsell color: 2.5Y 7/4–6/4) and for the scarcer presence of
214 scattered clasts. This unit is characterised by a 2BCk horizon with well-developed angular and sub-
215 angular blocky structure passing downward into 2Ck horizon. Rhizoconcretions are present only in
216 the 2BCk horizon. In comparison to the overlying Bk horizon (LU9), it has perceptible silt content,
217 and is particularly indurated (transition to petrocalcic horizon). The deepest part of the LU8 can be
218 considered as a transition to saprolite. The lower boundary of LU8 is not exposed at the base of the
219 studied outcrop section.

220 *4.2 Micropedology*

221 In thin section, the Bk horizon (LU9) is apedal with close to single spaced porphyric patterns,
222 locally chito-gefuric (Fig. 5A–H). The microstructure is controlled by voids (Fig. 4A). The porosity
223 pattern is dominated by channels (root and faunal), and subordinately by chambers and simple
224 packing voids; estimated total void space is 25-30%. The silty clay micromass has a dull yellowish
225 brown colour (PPL) with some local yellowish and dark mottles (Fig. 5B), and cloudy to opaque
226 appearance. The crystallitic b-fabric is combined with an undifferentiated b-fabric (Fig. 5E–H);
227 locally mono- and granostriated b-fabrics occur. Well-sorted and dominantly subangular quartz
228 grains dominate the coarse fraction (>10 μm); they are accompanied by feldspar (plagioclase),
229 muscovite and rare biotite minerals, generally weakly weathered. Heavy minerals are rare.
230 Compound mineral grains and rock fragments are frequent; they include medium- and coarse-sand
231 sized polycrystalline quartz (Fig. 5E) and metamorphic rock fragments (serpentinite). A few
232 mollusc fragments, partially weathered, were observed (Fig. 5A and C). Iron and iron-manganese
233 oxides occur as impregnative features (segregation into the soil matrix, nodules, hypo- and
234 quasisoatings). Typic and rare geodic nodules of different size (20 μm –1 mm in diameter; Fig. 5A,
235 B) are orthic, dark brown, moderately to strongly impregnated, and generally irregular. Rare
236 anorthic nodules have a sharp boundary with the soil matrix and dark brown colours (Fig. 5F); they
237 are probably inherited by the erosion of a former weathered horizon or paleosol (Brewer, 1976).
238 Calcite crystalline pedofeatures are segregated into frequent and large (160 μm to millimetre
239 diameter) intrusive infillings (dense incomplete and loose discontinuous), distributed throughout the

240 Bk horizon, and are juxtaposed with brownish redoximorphic features. They are composed by
241 equigranular anhedral micritic crystals and are located mainly in channels and large voids.
242 Crystalline micritic impregnative hypocoatings occur on voids (mainly on root channels, see
243 examples in Durand et al. 2010) together with coatings of mineral grains, rock and mollusc
244 fragments. Textural pedofeatures are rare ($\leq 2\%$) and show various indications of degeneration
245 (fragmentation, assimilation into the soil matrix). Three types of fragmented clay coatings (i.e.
246 papules, according Brewer, 1976) were observed: the first two are dusty, non-laminated, red and
247 orange yellowish in colour respectively (Fig. 5C, D, E and H). Their extinction patterns are virtually
248 absent. The third pure clay coatings are yellow and show sharp extinction bands between crossed
249 polarizers (XPL).

250

251 *4.3 Chemistry and mineralogy*

252 XRD and binocular microscope observations on different fractions, in agreement with
253 micropedology and pedological observations, show that the samples collected from LU8 and LU9,
254 are mainly composed by quartz, calcite and a minor amount of plagioclase, feldspar and micas. The
255 calcite is mostly due to the presence of pedogenic carbonates. According to Retallack (1990) these
256 carbonates can generally be called calcareous rhizoconcretions and calcareous glaebules (Brewer,
257 1964) or nodules (Bullock et al., 1985). More specific, sometime confusing, literature exists on the
258 description and genetic origin of pedogenetic carbonate in soil/loess profiles (e.g. Klappa, 1980;
259 Barta, 2011 and reference therein). The most abundant pedogenic carbonate identified in LU8 and
260 LU9 resembles “hypocoatings” (Fig. 4C, Barta, 2011). Hypocoatings indicate dry formation
261 environments and have probably the same age as the dust accumulation (Barta, 2011) and their
262 presence may refer to former patchy vegetation. The higher carbonate concentration could cement
263 hypocoatings together, which will act like a nucleus for later precipitation producing larger
264 concretions (i.e. nodules).

265 Qualitatively, the observations under binocular microscope showed that the basal samples are
266 coarser and contain arenitic clasts, rare eroded and partially altered small bioclast fragments of
267 marine molluscs and forams, and a minor amount of ophiolite clasts derived by the dismantling of
268 the substrate. These virtually disappear progressively upward and are completely substituted by a
269 fine-grained matrix dominated by angular to poorly rounded quartz grains, with rare land snail
270 shells, and with the carbonate fraction ranging from ca. 5 to 40 % (Fig. 6), with the lower values
271 found in the LU9.

272 The CaO and CaCO₃ contents (Fig. 6) show a high degree of correlation ($R^2=0.99$), which implies
273 CaO is mainly related to calcite precipitation and not from the bedrock (e.g. anorthitic plagioclase

274 and Ca-pyroxene). $\text{TiO}_2\text{-MnO-Fe}_2\text{O}_3$ are highly correlated, as are Fe_2O_3 and transition metals (V,
275 Cr, Co) (Fig. 6); because transition metals can be hosted in Fe-Mn-oxides, the transition metal
276 concentration can indicate the relative abundance Fe-Mn-oxides. However, the positive correlation
277 between Fe_2O_3 and MgO ($R^2=0.92$) can also indicate that these phases are probably related to the
278 variation of the content in the substrate rocks.

279 $\text{CaCO}_3\text{-Sr}$ are positively correlated ($R^2=0.91$) indicating that Sr is principally hosted in the CaCO_3
280 concretions. Ba and Sr are instead negatively correlated ($R^2=0.86$). This may be due to the different
281 partition coefficients of these trace element related to CaCO_3 for the progressive evolution of the
282 solution into the soil, dissolving and precipitating carbonate (Morse and Bender 1990), but it can
283 also be due to the fact that Ba could be mostly related to the mafic substrate. All these data indicate
284 the presence of a local clastic source, and an “exotic” one related, for instance, to abundant quartz,
285 and a secondary chemical deposition (pedogenic) related to CaCO_3 precipitation. The carbonate can
286 be directly precipitated by chemical weathering of Ca-rich minerals (e.g. White et al., 1999; Knauth
287 et al., 2003) but in the absence of carbonate rocks it can be related to the arrival of externally-
288 sourced carbonate, transported by winds (the so-called primary carbonate of loess deposits, Pécsi,
289 1990), which is then progressively dissolved/re-precipitated during pedogenetic processes.

290

291 *4.4 Stable isotopes*

292

293 Modern pedogenetic carbonates sampled in two localities along the Tuscan coast show a relatively
294 narrow isotopic variability (Figs. 1, 4A, 6; Table 2). The $\delta^{13}\text{C}$ ranges from -9.5 to -10.6 ‰ (mean -
295 10.2 ± 0.3 ‰), whereas $\delta^{18}\text{O}$ ranges from -3.7 to -4.9 ‰ (mean -4.4 ± 0.4 ‰). However, the two sites
296 show a small difference in their oxygen isotope values (ca. 0.7 ‰) possibly indicating small
297 differences in soil water evaporation with an ^{18}O -enrichment in the soil solution at Castiglioncello
298 (e.g. Cerling and Quade, 1993; Zanchetta et al., 2000). Significant differences in the mean
299 temperatures can be ruled out, as well as local differences of the isotopic composition of meteoric
300 precipitation (Longinelli and Selmo, 2003), which is quite constant along the Tyrrhenian coast and
301 around -5 ‰. The carbon stable isotope composition is in the range expected for soil supporting a
302 C_3 plant community (Cerling and Quade, 1993). Pedogenic carbonates in LU8 show a $\delta^{13}\text{C}\text{-}\delta^{18}\text{O}$
303 positive correlation ($R^2=0.76$), with $\delta^{13}\text{C}$ ranging from -5.8 to -8.9 ‰ (mean -7.6 ± 1.0 ‰) and $\delta^{18}\text{O}$
304 ranging from -4.4 to -2.5‰ (mean -3.5 ± 0.6 ‰). These figures indicate that important differences
305 exist between modern pedogenic carbonates and those within LU 8 (Figs. 4A, 6). Moreover, along
306 the section there is a clear and consistent variation, with higher $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values between 28,8
307 and 20 m a.s.l.

308

309 *4.5 The non-marine mollusc assemblage*

310 The non-marine mollusc assemblage is strongly oligotypical (e.g. Esu et al., 1989) and comprises
311 only four species of Gastropod pulmonata: *Pupilla muscorum* (LINNEUS 1758), *Vallonia pulchella*
312 (MÜLLER 1774), *Candidula unifasciata* (POIRET 1801) and *Jamina quadridens* (MÜLLER
313 1774). Because no significant changes occurred between different samples, we consider the total of
314 all samples. Number of specimens and percentages are reported in Table 4.

315

316 ECOLOGICAL GROUP 4 – STEPPE

317

318 This group includes the species which inhabit dry and sunny places like *Candidula unifasciata* and
319 *Jamina quadridens*. According to Adam (1960), Magnin (1993), and Kerney and Cameron (1999)
320 *C. unifasciata* is characteristic of dry, open rocky areas including dunes. It reaches 2000 m of
321 altitude in the Alps (Kerney and Cameron, 1999). Studies on French populations report *C.*
322 *unifasciata* as a “continental” species, avoiding typical Mediterranean climate (Pfenninger and
323 Magnin, 2001; Pfenninger et al., 2003).

324

325 *Jamina quadridens* is a xerophilous species which lives in sunny and open lands, upon herbaceous
326 and shrubby vegetation, especially on calcareous rocks. It is not very common in grassland with a
327 principal distribution over the Mediterranean (Kerney and Cameron, 1999).

328

329 This group is the most dominant, accounting for 80% of the assemblage, with *C. unifasciata* alone
330 accounting for 79% of the specimens.

331

332 ECOLOGICAL GROUP 5 – OPEN LANDS

333

334 This group includes the species living in open lands but with different requirements in terms of
335 humidity (Ložek, 1964, 1990). *Vallonia pulchella* is typical of open calcareous habitats, moist
336 meadows, marshes sand dunes and occasionally dry grasslands and screes (Kerney and Cameron,
337 1999). *Pupilla muscorum* is common in open spaces such as dry exposed calcareous places: screes,
338 stones walls, grassland, dunes (Adam 1960; Kerney and Cameron, 1999). It is commonly believed
339 to be resistant to low temperature and is frequently found in Pleistocene loess deposits of Central
340 Europe (Ložek, 1964, 1990; Puisségur 1976; Esu et al. 1989).

341

342 *4.6 Chronology*

343 OSL ages from Mauz (1999) and our ^{14}C dating are in agreement and indicate that this succession is
344 probably of Late Glacial age, being constrained by the basal coastal marine layers grossly
345 corresponding to late MIS5, and the age of the LU10 dated at 9.7 ± 2.4 ka by luminescence methods.
346 The two radiocarbon dates were obtained on carbonate concretions, appear in stratigraphic order
347 and suggest an age which may overlap with Late Allerød and Younger Dryas (YD) (Table 3), or
348 better with the GS -1 and GI-1 (Björck et al., 1998; Blockley et al., 2014). It is often assumed that
349 pedogenic carbonates in loess successions are formed synchronously with loess deposition but
350 radiocarbon dating of loess-paleosol sequences have shown that this is not necessarily the case
351 (Gocke et al., 2011). Therefore, in the later discussion is implicitly assumed that these radiocarbon
352 dating represent a minimum age for the deposits. Then, stable isotope composition of pedogenic
353 carbonates can give information at the time constrained by radiocarbon dating, but not necessarily
354 coincident with the time of loess deposition.

355

356 **5. Discussion**

357

358 The succession has a substrate formed by ophiolitic rocks, and the presence of abundant quartz and
359 white and black micas clearly indicates an external source of clastic material. One possible source
360 for these minerals would be the arenitic Macigno Formation extensively outcropping along this
361 sector of the coast (Lazzarotto et al., 1990). Given the local geomorphological conditions they can,
362 however, only be supplied by wind transport. Figure 7 shows the comparison between composition
363 of the Macigno Formation and LU9 and LU8 units for $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$ and $\text{Fe}_2\text{O}_3\text{-MnO-TiO}_2$
364 diagrams. It is evident they show significantly different compositions, representing the mixing of
365 different sources, even although the Macigno Formation probably represents one of the sources
366 forming the LU9 and LU8 units (e.g. Fig 7, $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$ diagram). A second source could have
367 originated by the local dismantling of the littoral arenites from the lower unit part of Buca dei Corvi
368 sections. LU4 is basically aeolian and the deposits of this unit could have outcropped well above the
369 present sea level. Indeed in the lower part of the analysed section, fragments of this unit are present.
370 However, tiny fragments of marine shells and clasts of the lower arenitic units are restricted only to
371 the two lower samples and disappear upwards. Therefore, dust transportation by wind is a
372 reasonable origin, even if the coarser fraction would have been supplied by local colluvium along
373 the slope from the local mafic bedrock.

374

375 In light of previous discussion, LU9-LU8 buried horizons reflect the land surface aggradation,
376 which occurred in a Mediterranean coastal area through both eolian and colluvial deposition,

377 progressively affected by pedogenic processes. The truncated upper limit indicates that soil-forming
378 processes were followed by an erosional phase, in agreement with the nature of the upper LU10.
379 The macromorphological and micromorphological analyses reveal that the main soil-forming
380 processes were characterized by calcite migration, re-precipitation and accumulation, so that the
381 LU9 horizon can be generically regarded as “Calcisol” (IUSS Working Group WRB, 2006).
382 Calcium carbonate-rich horizons are common in highly calcareous parent materials and widespread
383 in arid and semi-arid environments (IUSS Working Group WRB, 2006), indicating higher annual
384 evaporation and low annual precipitation. On the Earth surface today calcic soils develop in areas
385 receiving less than 1000 mm yr⁻¹ precipitation, with the great majority in areas of less than 800 mm
386 yr⁻¹ precipitation (Buck and Mack, 1995, Retallack, 2005). In addition, the presence of
387 redoximorphic features in the LU9 horizon points to a “short” period of water saturation (Lindbo et
388 al., 2010) and suggests that precipitation may have been seasonal (Buck and Mack, 1995).
389 Fragments of illuvial coatings occur in transported material or in soils with strong bioturbation
390 (Kühn et al., 2010): in this light it is possible to state that clay illuviation can be regarded as an
391 indicator of a former pedogenic phase taking place in a past environmental context, prior both to
392 pedoturbation (responsible for fragmentation of clay coatings) and to development of calcic features
393 (which are not compatible with clay dispersion required for clay illuviation, Kühn et al., 2010 - see
394 also Zerboni et al., 2011 for a similar sequence of processes).
395 The studied weathering horizon LU9 exhibits distinct evidence of relict soil processes that can be
396 referred to climatic conditions very different from the present; hence it can be considered as a
397 buried paleosol according to the Paleopedology Glossary by the INQUA Working Group on
398 “Definitions used in Paleopedology” (1995). The fact that the substrate is not carbonate is a further
399 argument for eolian deposition of carbonate, which is subsequently re-deposited along the soil
400 profile.

401
402 Non-marine faunal assemblage analysis complements the pedological observations. Overall, the
403 association indicates the presence of an open and dry area, probably with climate conditions colder
404 than the present day. This kind of association characterizes the cold and arid phases of the Middle to
405 Late Pleistocene in Central and Southern Italy (Esu, 1981; Esu et al., 1989; Esu and Girotti, 1991;
406 Di Vito et al., 1998; Marcolini et al., 2003; Sarti et al., 2005) and shares some common
407 characteristics with cold and arid phases of loess deposition of Europe (e.g. Ložek, 1964, 1990,
408 2001; Puisségur, 1976; Limondin-Lozouet and Antoine, 2001). However, the climatic indication is
409 not as extreme as in Central Europe given the presence of more thermophilous Mediterranean
410 elements like *J. quadridens*.

411 Although we have to take into account that radiocarbon ages of pedogenic carbonates can be
412 susceptible to several concerns such as incorporation of old carbonate and/or dissolution and
413 carbonate redeposition, and the possible absence of contemporaneity of pedogenic carbonate with
414 the deposit, the dates reported here are generally consistent with the hypothesis that most of LU9-8
415 would have developed during the Late Glacial (Table 3). This is further constrained by the OSL
416 date of 9.7 ± 2.4 (Maunz, 1999) from LU10.

417 Regional arboreal pollen reconstructions indicate during the Late Glacial a larger presence of
418 vegetation typical of open spaces compared to the Holocene (Fig. 8, e.g. Ramrath et al., 2000;
419 Brauer et al., 2007; Allen and Huntley, 2009).

420 Qualitatively, the oxygen isotopic composition of pedogenic carbonate from LU8 and LU9 is
421 generally ^{18}O -enriched compared to present day-forming pedogenic carbonate in coastal Tuscany.
422 As reported for other continental carbonates forming in different Mediterranean regions (e.g.
423 Zanchetta et al., 2000, 2005; 2006, 2007a,b, 2015; Roberts et al., 2008; Regattieri et al., 2014, 2015,
424 2016), high $\delta^{18}\text{O}$ values can be associated to dry conditions. This can be related to several factors in
425 combination, including increasing evaporation (e.g. Zanchetta et al., 1999; 2000, 2007a; Roberts et
426 al., 2008), decrease in the amount of precipitation (Bard et al., 2002; Zanchetta et al., 2007a,b,
427 2014; Regattieri et al., 2015, 2016) and/or changes in the provenance of the precipitation (Zanchetta
428 et al., 2007a,b).

429 Using Cerling's (1984) data on modern soils, Jiamao et al. (1997) proposed the following
430 relationship between $\delta^{18}\text{O}$ values in water and soil carbonate, which incorporates the evaporative
431 effect in soils (Zanchetta et al., 2000):

432

$$433 \delta^{18}\text{O}_{\text{H}_2\text{O}} = -1.361 + 0.955 \delta^{18}\text{O}_{\text{CaCO}_3} \quad (R^2 = 0.98)$$

434

435 Overall, modern soil carbonates of this study (data in Table 2) yield $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ of -5.6 ± 0.4 ‰, which
436 is in very good agreement with modern rainfall $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values observed along the Tyrrhenian coast
437 of Italy (ca. -5.5 ‰; Longienelli and Selmo, 2003). Our results indicate that Jiamao's equation is a
438 robust predictor of $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values also for the studied area. The $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values for LU8 and LU9
439 carbonates range from -3.9 ‰ to -5.5 ‰, with an average value of -4.7 ± 0.6 ‰. On average, this
440 implies meteoric waters enriched by ca. 1 ‰ compared to present day. Bard et al. (2002) reported
441 for the area an amount effect in precipitation of ca. -2 ‰/100 mm/month for the oxygen isotopic
442 composition, which in our case could indicate a decrease in precipitation of ca. 50 mm/month for
443 the period. However, this estimate does not incorporate changes in the average $\delta^{18}\text{O}$ values of the
444 oceans due to variations in the ice volume during deglaciation (the so-called source effect). For

445 example, according to Lambeck et al. (2014) the eustatic sea level for the considered time interval
446 would have ranged from ca. -40 to ca. -80 m below present day sea level (Fig. 8, Lambeck et al.,
447 2014). Using a coefficient of 0.009 ‰/m^{-1} for the effect of eustatic sea level on the average $\delta^{18}\text{O}$
448 value of oceans (Lambeck et al., 2014; Rohling et al., 2014; Shakun et al., 2015), a sea level stand
449 between ca. -40 to -80 m would have promoted a change in the average $\delta^{18}\text{O}$ value of the oceans of
450 from $+0.36 \text{ ‰}$ to $+0.72 \text{ ‰}$. This may suggest that part of the isotopic enrichment could be due to
451 changes in the isotopic composition of the oceans. We have also to consider that the Mediterranean
452 is a “concentration” basin in which the isotopic composition of sea water is higher than the ocean
453 average (Pierre, 1999; Emeis et al., 2000). However, isotopic data (Figs. 6,8), are not consistent
454 with a significant source effect. This would be expected to be more pronounced for the lower (and
455 so older) samples, which is not the case. Therefore, $\delta^{18}\text{O}$ values are most likely indicative of drier
456 conditions, characterised by higher $\delta^{18}\text{O}$ in meteoric precipitation probably related to decrease in
457 the amount of precipitation.

458

459 The average value of the $\delta^{13}\text{C}$ of modern pedogenic carbonate is $-10.2 \pm 0.3 \text{ ‰}$, significantly lower
460 than Late Glacial pedogenic carbonate ($-7.6 \pm 1.0 \text{ ‰}$). This difference can be due to different factors.
461 Indeed, the carbon isotope composition of pedogenic carbonates ultimately derives from the
462 isotopic composition of soil CO_2 , which depends on soil respiration rate and the amount and
463 typology of vegetation (Cerling and Quade, 1993). Therefore, higher values are consistent with
464 lower respiration rate and/or changes in the proportion of C_3/C_4 and/or simple changes in ratio
465 between shrubs/herbs/trees, with trees having usually the lower isotopic composition (e.g. Masi et
466 al., 2013a,b). Lower respiration rate and increase in C_4 are both indicators of drier conditions (Raich
467 et al. 1992), even though C_4 are also adapted to higher temperature (Deines, 1980).

468 According to Wang and Zheng (1989) the proportion of C_4 plants (x) can be calculated using the

469 equation:

$$470 \quad x = (11.9 + \delta^{13}\text{C}_{\text{CaCO}_3})/14$$

471 According to this calculation, the Late Glacial would be characterized by larger proportion of C_4
472 vegetation (ca. 30%) compared to present day (ca. 11%). For instance, this could be due to the
473 increase of grass and sedge, which include species having C_4 photosynthesis in particular in
474 Amaranthaceae and Chenopodiaceae (e.g. Ehleringer et al., 1997).

475 However, these estimations are based on the assumption that C_3 plants have a mean carbon isotopic
476 value of ca. -27 ‰ , whereas in the Mediterranean C_4 vegetation is rare and restricted to some
477 specific environments (Colonese et al., 2014), and carbon isotopic composition of C_3 vegetation in

478 drier environments can be significantly higher than the average (e.g. Kohn , 2010; Diefendorf et al.,
479 2010; Masi et al., 2013a,b). In the Mediterranean, significant differences are observed in water-use
480 efficiency which varies largely between evergreen and deciduous species (e.g. Valentini et al.,
481 1992) and also seasonally (Filella and Peñuelas, 2003). So the estimation of the amount of C₄ is
482 probably too high. Breecker et al. (2009) observed that pedogenic carbonates in dry environments
483 form during warm, dry periods and do not record mean growing season conditions as typically
484 assumed. Therefore, pedogenic carbonate provides a C₄-biased record of paleovegetation, especially
485 in dry soils. Accordingly, higher values recorded in the LU8 and LU9 units compared to present
486 pedogenic carbonates reasonably indicate soil conditions characterized by lower respiration rate in a
487 drier climate (e.g. Raich et al. 1992), with vegetation composition different from present conditions.
488 However, a comment is necessary for the high linear correlation observed between $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$ in
489 Late Pleistocene carbonates (Fig. 4, $R^2=0.76$). If also modern data are included the correlation still
490 appears high ($R^2=0.71$). This high correlation can be explained in different ways. Considering that
491 the regression line has equation for LU8 and LU9:

492

$$493 \delta^{13}\text{C}=0.506 \delta^{18}\text{O} + 0.323$$

494

495 this means that the regression line passes close to the origin of the axes with an isotopic
496 composition resembling that of marine carbonate (e.g. Land, 1989). Therefore, a mixing with a
497 clastic marine component could be possible. Assuming a simple mixing model with two end
498 members: the isotopic composition of marine carbonate (close to 0‰) and the modern “pure”
499 pedogenic carbonate composition, the highest values of late Pleistocene pedogenic carbonate would
500 be produced by a mixing ratio of ca. 50% with marine carbonate. Different values would be
501 obtained using a higher isotopic composition of the clastic marine component (Land, 1989). In any
502 case, if the clastic contamination were so high, any calculation of past vegetation and/or isotopic
503 composition of meteoric water would be unreliable. However, this scenario is unlikely. Indeed,
504 there is no evidence of so large a clastic carbonate amount in the sediment: very rare marine
505 fragments in the >1 mm fraction are observed only at the base of the outcrop. No other clastic
506 carbonate was detected. Moreover, if fragments of marine shells were the source of contamination,
507 this would be detected by the presence of traces of aragonite in the XRD, which is not the case; and
508 finally, petrographic observation did not support large amounts of clastic carbonate.

509 A more likely explanation for the isotopic covariation is related to the climatic effect. For instance it
510 has been observed in speleothems of central Italy that $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$ positive correlation can be driven
511 by climatic effects (e.g. Drysdale et al., 2004; Zanchetta et al., 2007a,b, 2015; Regattieri et al.,

512 2014a,b). Increasing carbonate $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are related to decrease in precipitation and
513 decrease of CO_2 production in soils for the drier conditions. Moreover, low respiration rate in drier
514 environments can favor a deeper penetration of atmospheric CO_2 within the top soil (Cerling and
515 Quade, 1993). Low precipitation, as discussed earlier, can produce organic matter with higher $\delta^{13}\text{C}$
516 values, as well as higher $\delta^{13}\text{C}$ values of respired CO_2 . A positive correlation, even if mediated by
517 other factors, has also been observed in lacustrine carbonate of the same region and interpreted as
518 changes in soil productivity during drier and colder intervals accompanied by higher $\delta^{18}\text{O}$ values of
519 water for changing composition of meteoric precipitation and increasing evaporation (Regattieri et
520 al., 2015, 2016; Giaccio et al., 2015).

521 Despite potential limitation of accuracy and precision related to the material dated, the available
522 chronology consistently indicates that LU8 and LU9 may have formed during the Late Glacial, in
523 drier conditions compared to present day. For this period pollen data from Monticchio (Brauer et
524 al., 2007), oxygen isotope composition from Corchia cave (Zanchetta et al., 2007b; Regattieri et al.,
525 2014) and sea surface temperature from ODP976 (Martrat et al., 2014), suggest more drier and
526 colder condition than in the Holocene (Fig. 7). These data are compared to the NGRIP record as
527 extra-regional reference data. Over the central Apennine area loess deposition is interrupted with
528 the onset of the Bølling-Allerød time interval, as constrained by tephra layers (Giraudi et al., 2013,
529 Fig. 8). We can speculate that the possibility of dust accumulation on the coastal area for a longer
530 period compared to the Apennine is probably related to the fact that the continental platform was
531 still exposed by the low sea level stand (Fig. 8), representing the deflation area for the sediment, in
532 a context where vegetation and soil had not completely recovered.

533

534 **6.Summary and Conclusions**

535

536 Lithological, pedological and geochemical data support the presence of pedogenically altered loess
537 deposits at the top part of the Buca dei Corvi succession as reported by Ottman (1953). These
538 deposits were partially colluviated and mixed with fragments originating from the local substratum.
539 Chronologically (at least for the exposed part) they likely have accumulated during the Late Glacial
540 and/or experienced pedogenic alteration during this period. Non-marine mollusc assemblage,
541 pedogenic features and stable isotopes of pedogenic carbonates indicate environmental conditions
542 drier than the present day and characterized by sparse vegetation. Using the $\delta^{18}\text{O}$ values of modern
543 pedogenic carbonates for calculating present day $\delta^{18}\text{O}$ values of meteoric precipitation with the
544 Jiamao et al. (1991) equation, yielded values consistent with measured local meteoric precipitation,
545 indicating that this equation is robust also for the area and useful for reconstructing quantitatively

546 past isotopic composition of rainfall. Carbon isotopic composition indicates a higher proportion of
547 C₄ plants (possibly related to an increase of herbs in vegetation) and/or decrease in soil respiration
548 rate. An increase in the isotopic composition of C₃ vegetation component due to more hydrological
549 stress could also have produced ¹³C-enriched soil organic matter and then a more ¹³C-enriched soil
550 CO₂ (Deines, 1980).

551 Most of the raised-marine terraces over the Tyrrhenian coast have been simply utilized for
552 reconstruction of relative high stand paleosealevel and/or tectonic movement with respect to a
553 certain expected eustatic sea level (e.g. Mauz, 1999; Nisi et al., 2003). This work has demonstrated
554 that more information can be obtained for characterizing low stand conditions and climate
555 deterioration, and the terraces can be useful archives for reconstruction of coastal evolution.
556 Moreover, this work suggests that distribution of loess deposits can be extended in the future to the
557 Tyrrhenian coast, in a more southerly position than previously documented.

558

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567

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942

943

944

945 Figure and table captions

946

947

948 Figure 1. Location Map

949

950 Figure 2. Stratigraphy of the Buca dei Corvi section (after Ciulli, 2005). Ages are reported as ka.

951 See text for detailed description.

952

953 Figure 3. Upper section of Buca dei Corvi section. (A) Panoramic view of the top of the Buca dei
954 Corvi-section, and the relationship between the lithostratigraphic units and the major bounding
955 surfaces. (B) Measured sedimentological log (modified from Ciulli, 2007). See Figure 1 for
956 location.

957

958 Figure 4 (A) $\delta^{18}\text{O}$ vs $\delta^{13}\text{C}$ of pedogenic carbonate from Buca dei Corvi section and modern
959 pedogenic carbonate from coastal Tuscany. For LU8 and LU9 hypocoatings and nodules are
960 reported separately; (B) Concretion from modern soil; (C) Hypocoatings from LU9. Black bars in
961 (B) and (C) correspond to 1 cm.

962

963 Figure 5. LU9 weathering profile, horizon BCK, thin section. (A) Channel microstructure associated
964 to a high porosity; orthic nodules (red arrows) and mollusc fragment (black arrow); Ch=chamber;
965 Cl=channel-PPL. (B) Close to single spaced porphyric c/f related distribution with dominant coarse
966 quartz grains embedded in a yellowish brown to brown micromass; strongly impregnated typic
967 nodule (white arrow)-PPL. (C) Ferruginous internal hypocoating on a shell fragment and dark
968 brown Fe-Mn segregations into the matrix; isolated reddish fragment of clay coating incorporated in
969 the groundmass (red arrow)-PPL. (D) Different generations of fragmented clay coatings
970 incorporated in the groundmass: pure clay coatings are yellow (black arrows) while dusty clay
971 coatings are reddish (red arrow)-PPL. (E) Unweathered quartz grains, rock fragments and poorly
972 weathered primary mineral grains dominate the coarse particle size fraction; dense incomplete
973 calcite infillings locally impregnated by brownish ferruginous segregations-XPL. (F) Complex c/f
974 related distribution: close to single spaced porphyric, locally chito-gefuric; strongly impregnated,
975 typic anorthic nodule (white arrow) and shell fragment (red arrow)-XPL. (G) Loose discontinuous
976 calcite crystalline pedofeatures within a large channel; crystallitic b-fabric is common in

977 correspondence with large concentrations of calcite in the fine fraction–XPL. (H) Fe-Mn
978 impregnations on dense incomplete calcite infillings, up to 4 mm thick; fragment of reddish dusty
979 clay coatings (white arrow)–XPL.

980

981 Figure 6. Geochemical and isotopic data from Buca dei Corvi section

982

983 Figure 7. Comparison between chemical composition of Macigno Formation and LU8 and LU9
984 deposits from Buca dei Corvi section. Macigno data from Lezzerini et al. (2008) and Gioncada et al.
985 (2011).

986

987 Figure 8. From the top to the bottom: Relative sea level (Lambeck et al., 2014); $\delta^{18}\text{O}$ of stalagmite
988 CC26 from Corchia Cave (Zanchetta et al., 2007b); $\delta^{18}\text{O}$ from NGRIP ice core (NGRIP members,
989 2004); Monticchio pollen data (Brauer et al., 2007); SST from core ODP 976 (Martrat et al., 2014).
990 Radiocarbon dating, this work; OSL dating from Mauz (1999); chronology of the end of deposition
991 of loess in Apennine (Giraudi et al., 2013).

992

993 Table 1. Stable isotope results from hypocoatings (°) and nodules (*) from Aurelia section (LU9
994 and LU8). Note that there are not systematic differences between the different kinds of carbonate
995 concretions.

996

997 Table 2. Stable isotope composition of modern rhizoconcretions collected at Baratti and
998 Castiglioncello (see Fig. 1). Concretions were collected along living roots in the modern soils.

999

1000 Table 3. Radiocarbon dating of concretions along LU8 and LU9. Calibration was performed using
1001 INTCAL13 database (Reimer et al., 2013).

1002

1003 Table 4. Via Aurelia section non-marine mollusc species grouped by ecological classes; number of
1004 specimens and their percentages are indicated. Ecological classes: 4 - steppe species; 5 - open land
1005 species.

Highlights

A multiproxy environment reconstruction from Late Glacial deposit of Central Italy is proposed;

Pedogenic features, land snail association and stable isotopes indicate dry climate condition;

$\delta^{18}\text{O}$ values of pedogenic carbonates indicates that $\delta^{18}\text{O}$ of precipitation was higher than present.

Table

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Sample	Depth (m a.s.l.) ¹	$\delta^{13}\text{C}$ ‰ (V-PDB)	$\delta^{18}\text{O}$ ‰ (V-PDB)
BCA10/1°	28.30	-8.93	-3.88
BCA10/2°	“	-8.60	-3.96
BCA10/3*	“	-8.27	-3.82
BCA9/1°	28.00	-8.39	-3.52
BCA9/2°	“	-8.68	-3.40
BCA9/3*	“	-7.34	-3.21
BCA8/1°	27.7	-6.52	-2.85
BCA8/2°	“	-5.82	-2.51
BCA8/3°	“	-6.52	-2.77
BCA7/1°	27.4	-6.51	-2.99
BCA7/2°	“	-6.69	-2.95
BCA7/3*	“	-6.26	-2.75
BCA6/1°	27,10	-6.65	-3.04
BCA6/2°	“	-6.52	-3.15
BCA6/3*	“	-6.00	-2.75
BCA5/1°	26.90	-6.92	-3.46
BCA5/2°	“	-7.17	-3.16
BCA5/3*	“	-6.87	-3.46
BCA4/1°	26.60	-7.62	-3.74
BCA4/2°	“	-8.54	-4.03
BCA4/3*	“	-8.55	-4.78
BCA3/1°	26.30	-8.61	-4.41
BCA3/2°	“	-8.85	-4.02
BCA3/3*	“	-8.96	-4.70
BCA2/1°	25.25	-8.75	-3.76
BCA2/2°	“	-8.09	-3.94
BCA2/3*	“	-7.41	-3.43

°Carbonate hypocoatings

*Carbonate nodules

See figure 4 for the position of the sampled section

<i>Locality/Label</i>	$\delta^{13}\text{C}$ ‰ (V-PDB)	$\delta^{18}\text{O}$ ‰ (V-PDB)
<i>Castiglioncello</i>		
Cast-1	-10.48	-4.17
Cast-2	-10.53	-4.02
Cast-3	-10.49	-4.08
Cast-4	-10.48	-3.74
Cast-5	-10.59	-3.97
<i>Baratti</i>		
Bar16	-10.07	-4.76
Bar15	-10.05	-4.69
Bar10	-10.39	-4.82
Bar9	-10.35	-4.52
Bar8	-10.31	-4.57
Bar7	-10.5	-4.47
Bar6	-9.90	-4.62
Bar5	-9.53	-4.89
Bar3	-9.77	-4.73

Sample	Laboratory code	Conventional Radiocarbon Age (yr BP)	Calibrated Radiocarbon Age ($\pm 2\sigma$) (Median probability)	$\delta^{13}\text{C}$ (‰ V-PDB)
BCA D.6 (28.2 m a.s.l.)*	Beta-235367	9980 \pm 50	11253 – 11629 (11440)	-7.6
BCA.D.4 (27.7 m a.s.l.)*	Beta-235368	11310 \pm 50	13074 – 13268 (13161)	-5.3

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Ecological Group	Species	Number of specimens	Percentage (%)
4	<i>Candidula unifascita</i>	1224	79
4	<i>Jamina quadridens</i>	17	1
<i>Sub-total</i>		<i>1241</i>	<i>80</i>
5	<i>Pupilla moscorum</i>	182	12
5	<i>Vallonia pulchella</i>	126	8
<i>Sub-total</i>		<i>308</i>	<i>20</i>
Total		1549	100

Figure
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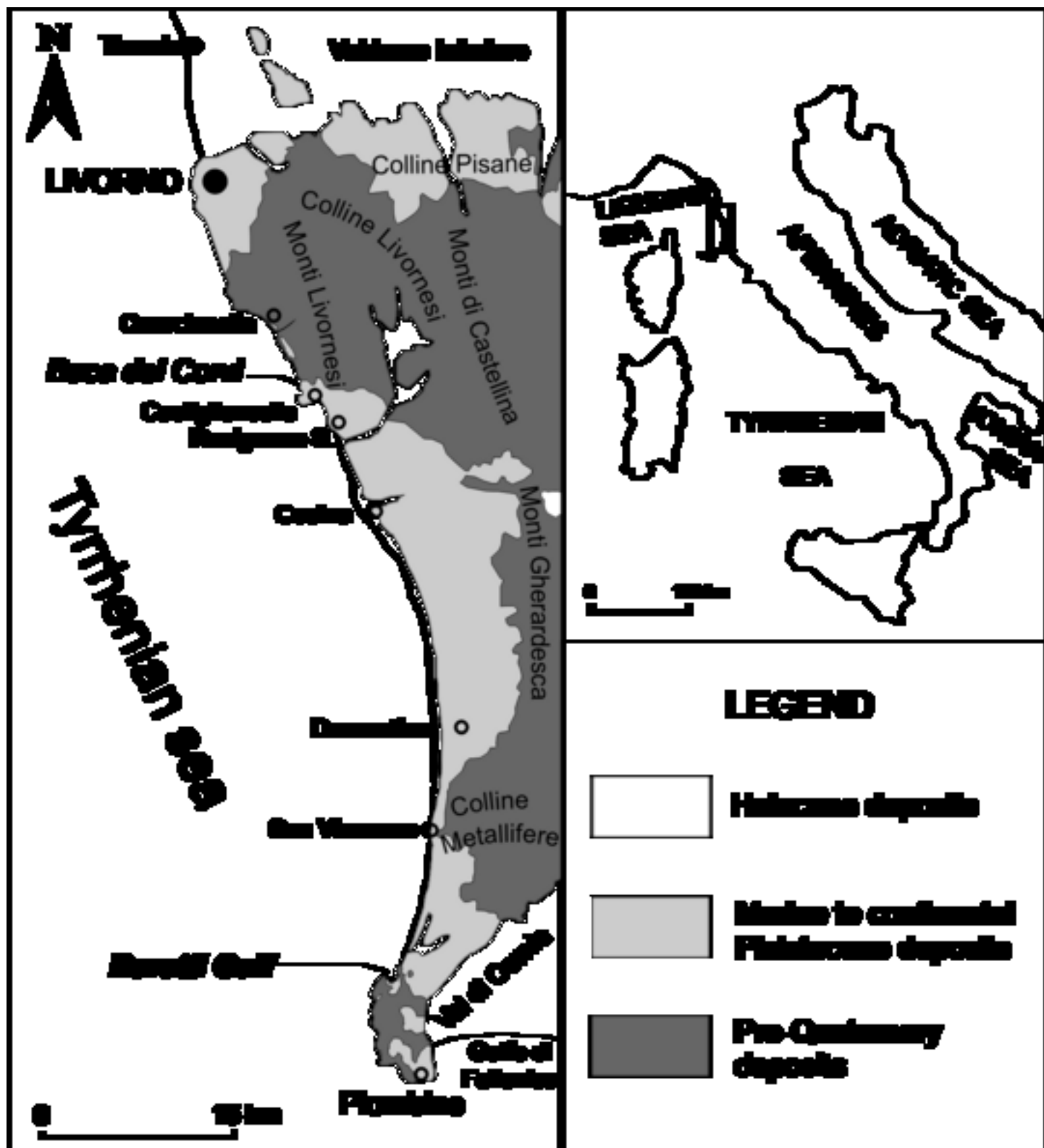
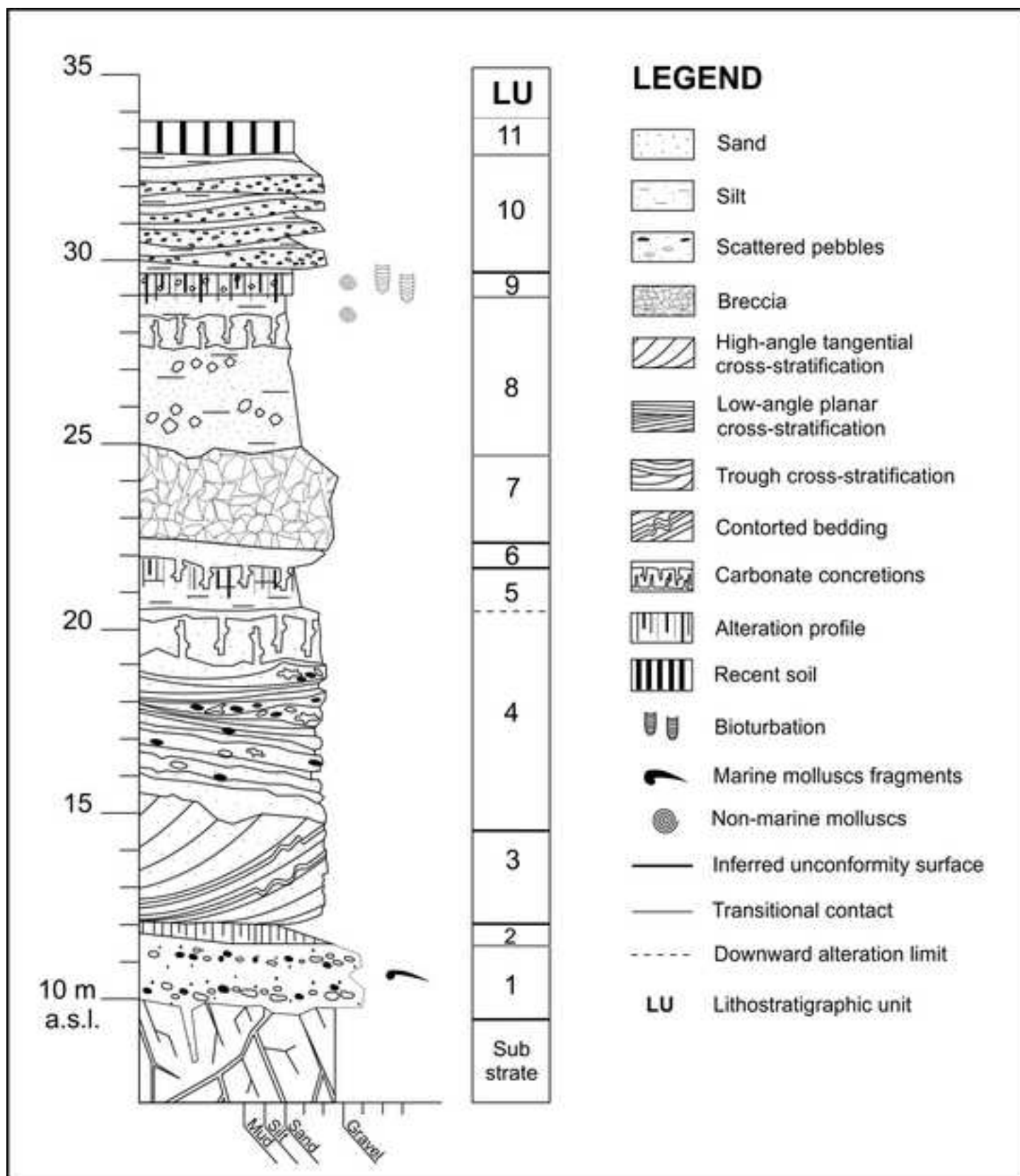


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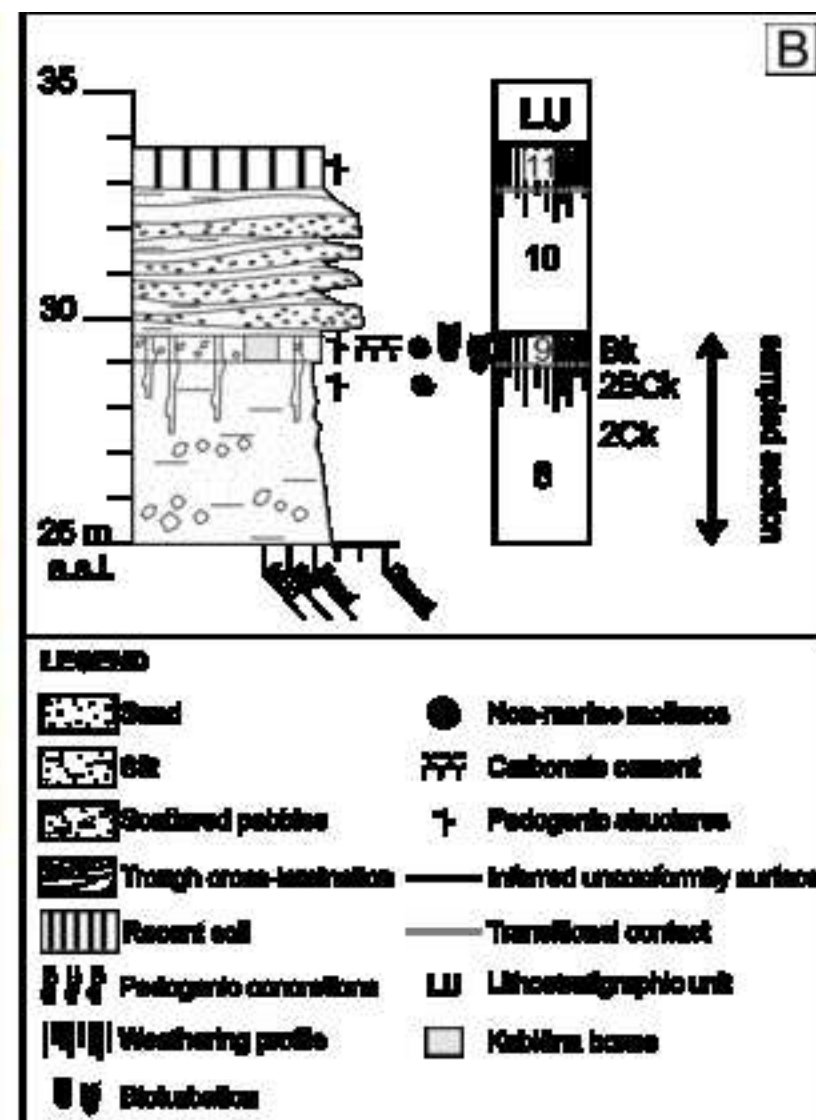
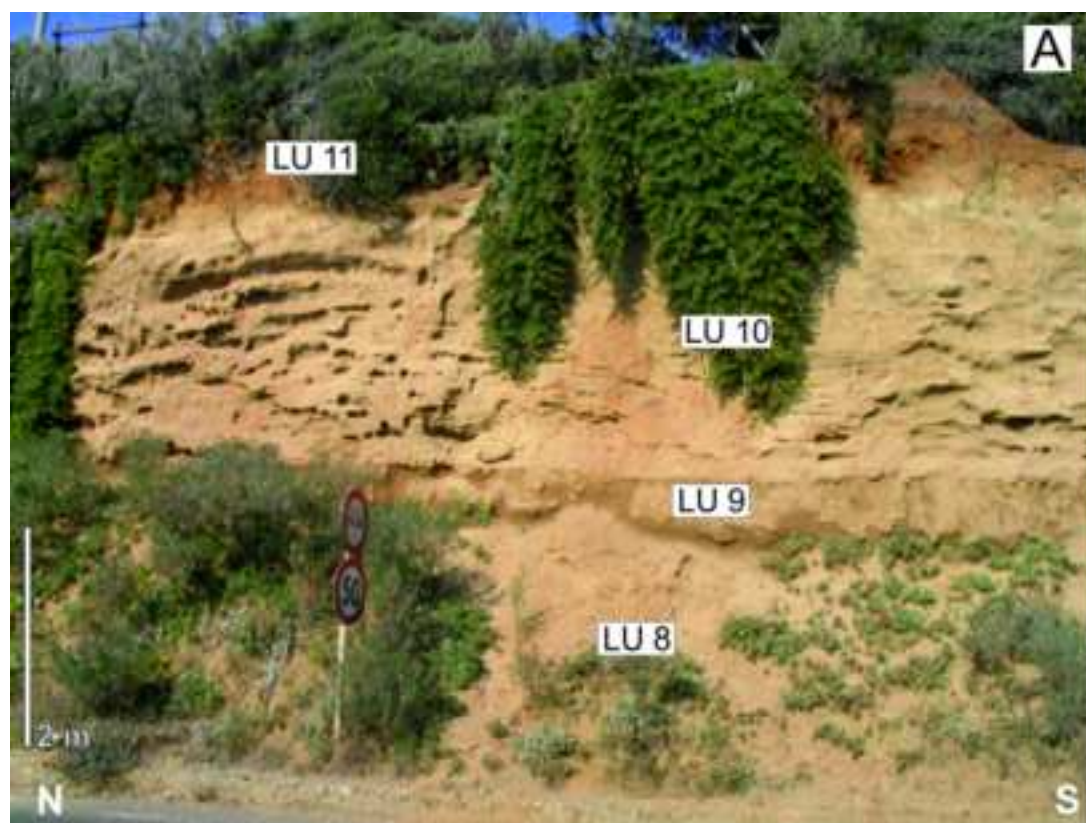


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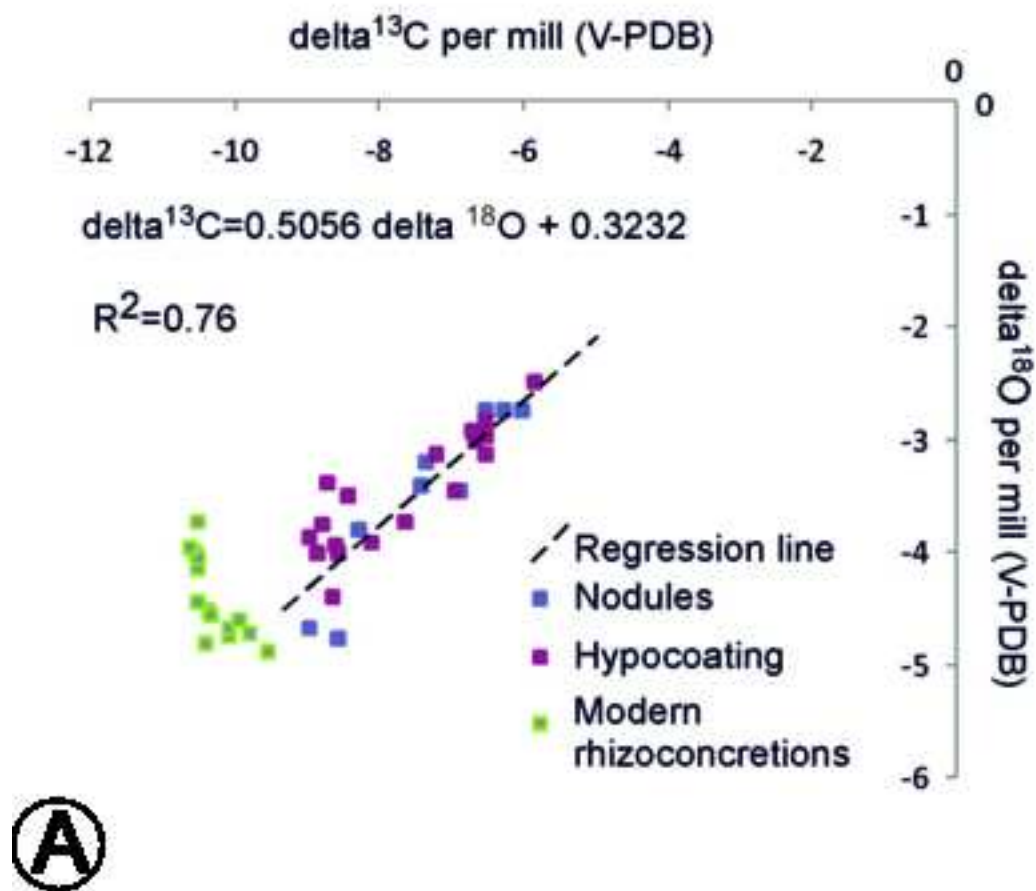


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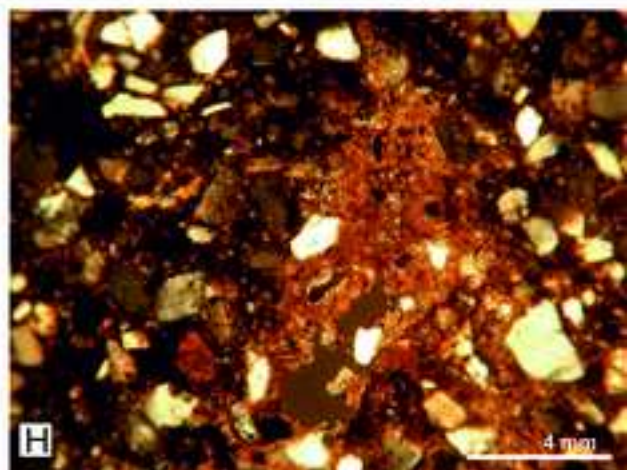
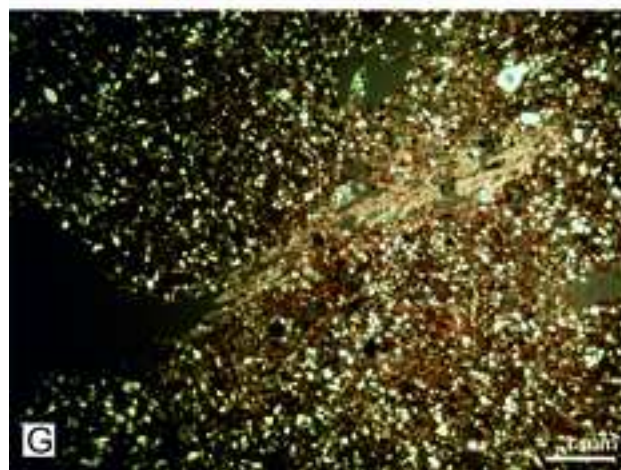
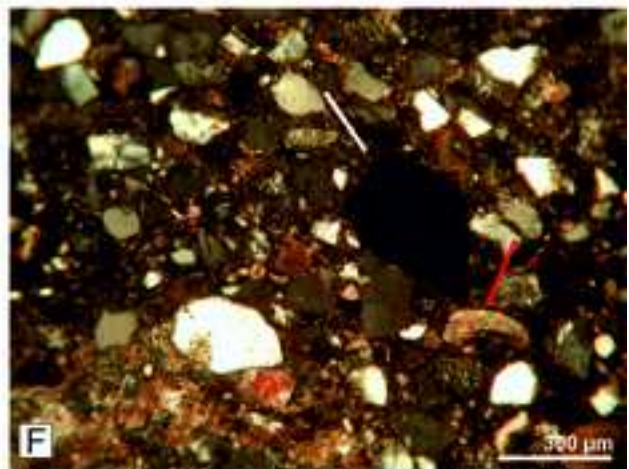
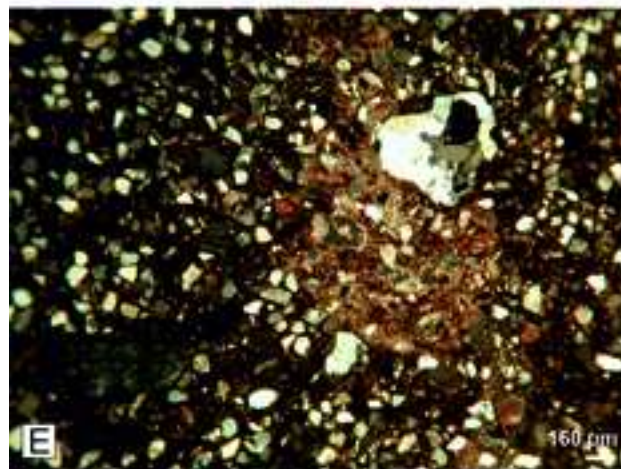
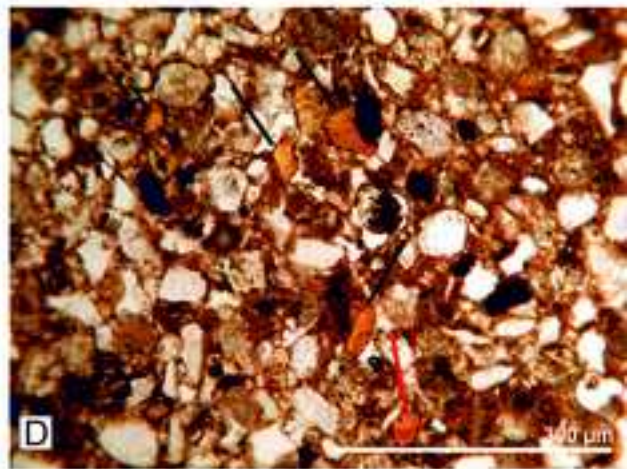
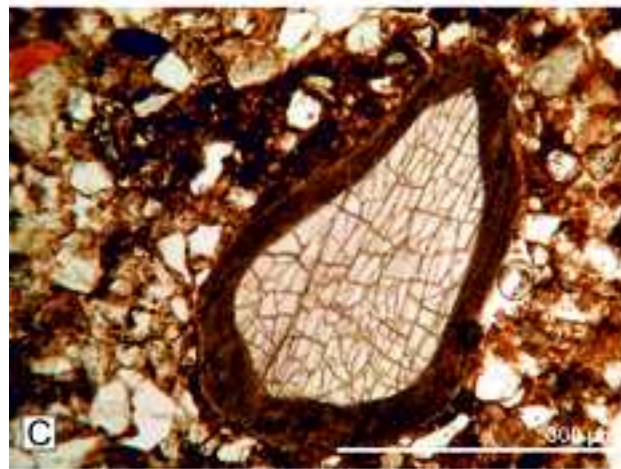
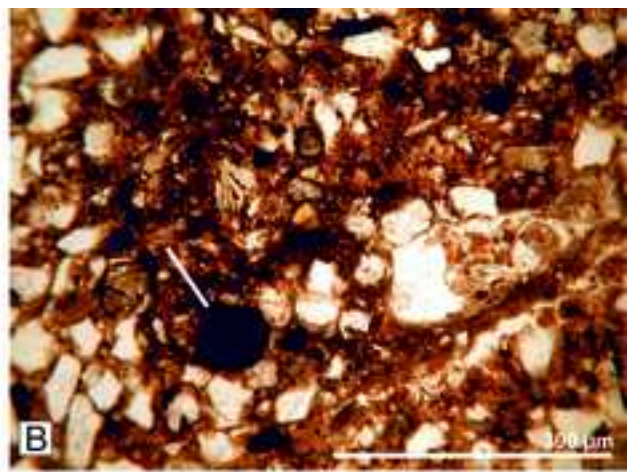
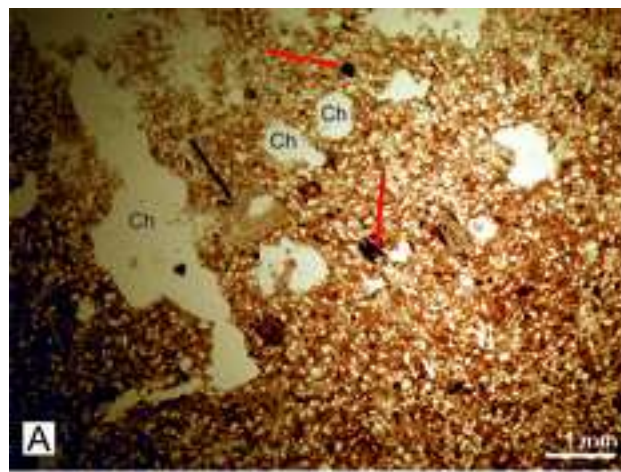


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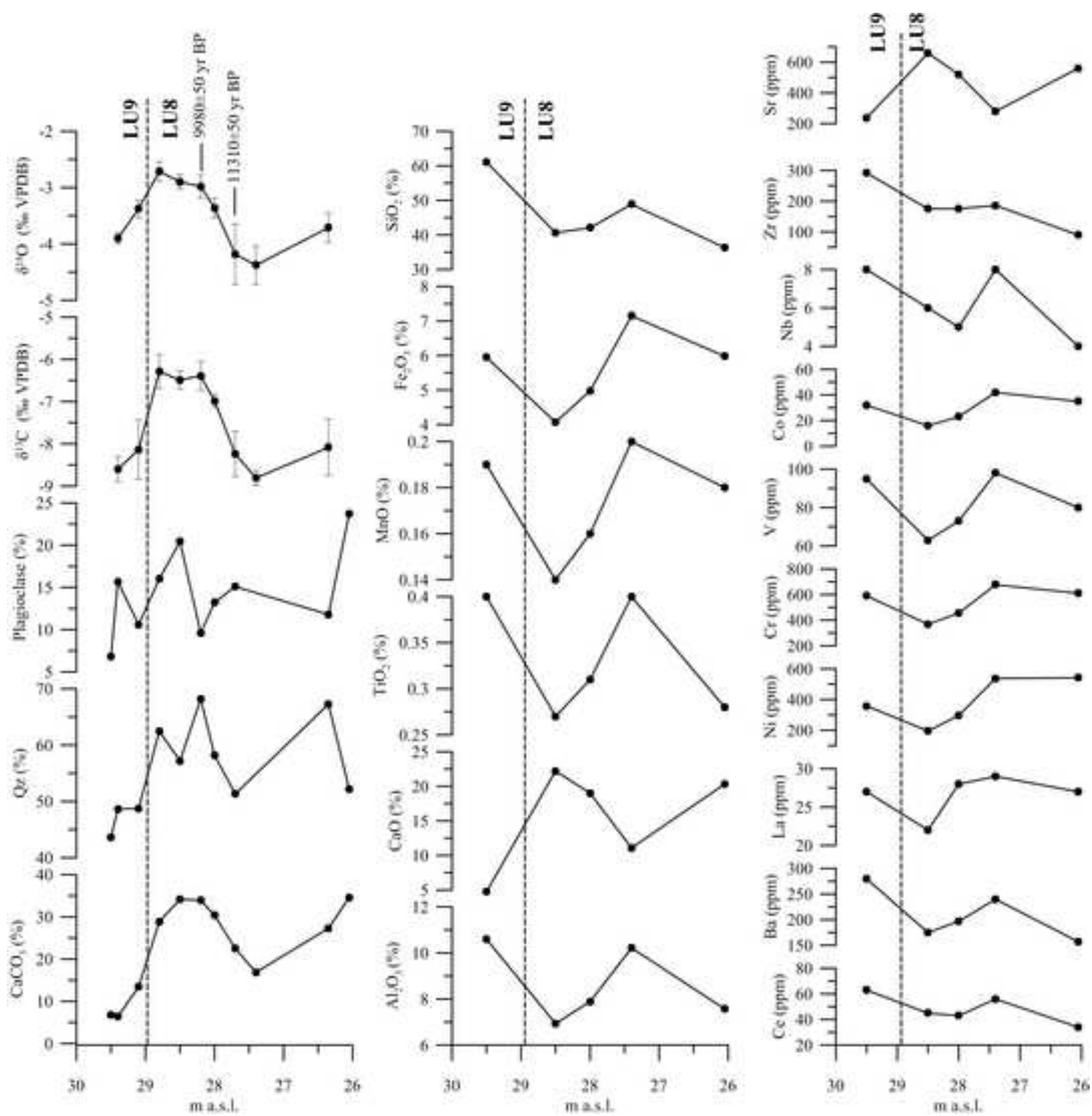


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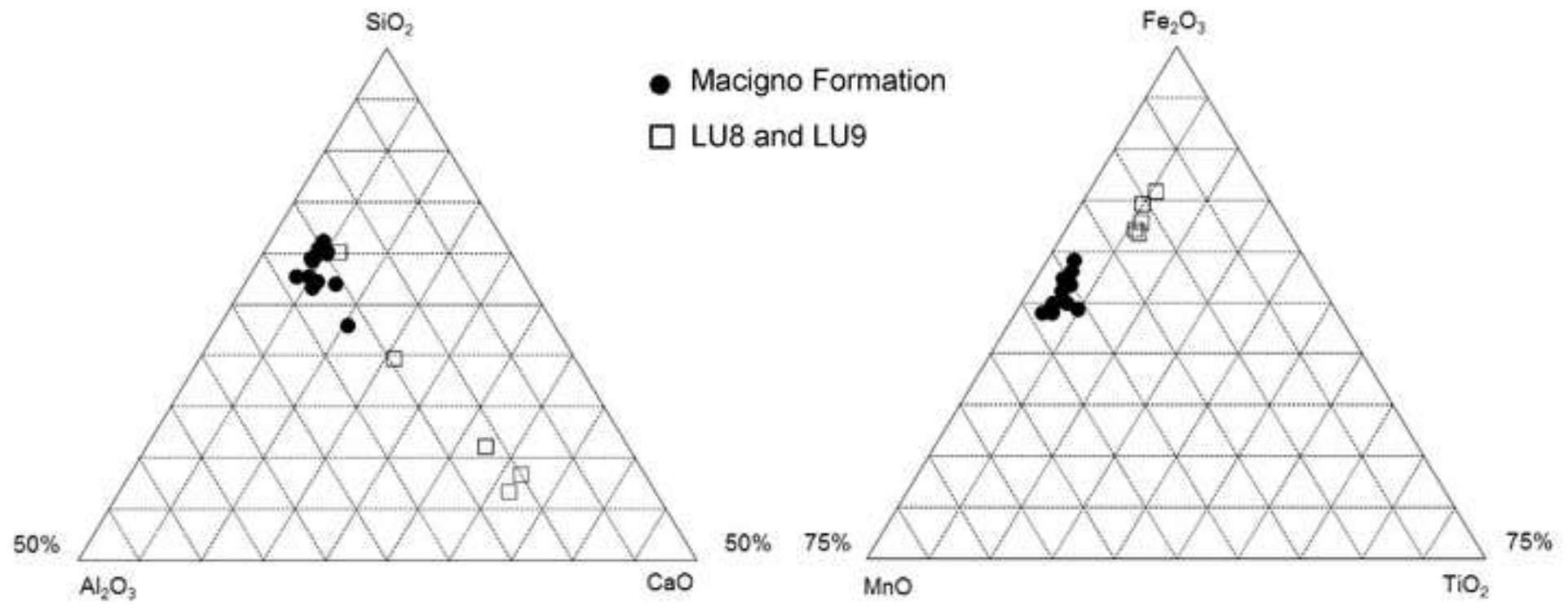


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