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1 Mineralogy and crystallization patterns in conodont bioapatite from first occurrence
2 (Cambrian) to extinction (end-Triassic)~~Mineralogy and crystallization pattern in~~
3 ~~conodonts: changes in bioapatite through the stratigraphic breadth of the conodont~~
4 ~~fossil record~~

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15
16
17 **ABSTRACT**

18
19 Bioapatite represents an important acquisition in the evolution of life, both in the seas and ~~over the on~~
20 ~~lands~~. Vertebrates applied calcium-phosphate biominerals to grow their skeletal support and to shape their
21 teeth, while some invertebrates sheltered their soft parts within apatite shells. Conodonts were the first
22 among vertebrates to experiment with skeletal biomineralization ~~with of~~ tooth-like elements in their
23 feeding apparatus. Spanning a time record of over 300 million years, they offer a unique tool to test
24 possible variation in bioapatite structure from the experimentation of a very primitive biomineralization
25 type to a more evolute pattern just before ~~getting going~~ extinct. X-ray microdiffraction carried out through
26 an X-ray micro-diffractometer, integrated with environmental scanning electron microscopy coupled with

chemical microanalyses (ESEM-EDX), has been applied in this study to investigate conodont ~~structural~~
~~investigation~~element crystal structure throughout the entire stratigraphic range of ~~conodonts~~these
organisms. In particular, bioapatite crystallographic cell parameters have been calculated for about one
hundred conodont elements ranging from the late Cambrian to the Late Triassic. Resulting data clearly
indicate two distinct distribution plots of cell parameters for paraconodonts and euconodonts. In contrast,
age, taxonomy, geographic provenance and CAI do not affect the dimension of the bioapatite crystal cells.
Conodont bioapatite crystallographic cell parameters have been compared with cell parameters resulting
from phosphatic/phosphatized material (ostracodes, brachiopods, bryozoans, and fish teeth) present in the
same residues producing conodonts. Resulting values of the cell parameters are, in general, mainly
correlated with the type of organisms even if, for some of them, a correlation also with age cannot be
completely ruled out. According to our data, primary bioapatite appears to imprint a key ~~role~~signature ~~in~~
on fossil crystal-chemistry (crystal structure and major chemical element contents), while the contribution
of fossilization and diagenetic processes seems less relevant.

Keywords: Paraconodonts; euconodonts; microdiffraction; cell parameters; biomineralization.

1. Introduction

Several present and fossil organisms, among both invertebrates and vertebrates, share the use of
bioapatite for the formation of their mineralized structures. Bioapatite has peculiar features that make it
suitable to act as a structural support for the body (skeleton), to allow mechanical grinding (teeth), and to
provide protection for the soft tissues (e.g., shell in brachiopods and skull of vertebrates) (Kallaste and
Nemliher, 2005; Pasteris et al., 2008; Liu et al., 2013). Furthermore, bioapatite is an important reserve for
phosphorus, a fundamental element for life that is also present ~~also~~ in biological molecules such as DNA,
RNA and many proteins, and is one of the main components of ATP (adenosine triphosphate), an essential
molecule for the metabolism of living organisms.

Biom mineralized structures in biological systems are made up of an organic and an inorganic component. The latter is typically nanocrystalline (10^{-9} m), with nanometric assemblies of atoms with dimensions ranging from ions (10^{-10} m) to macroscopic forms (Banfield and Zhang, 2001). However, there are significant differences between teeth and bones. Teeth are in fact provided with cells completely different from those involved in ossification processes, being odontoblasts specialized in the dentin formation process and ameloblasts in the formation of the enamel. Dentin consists of collagen and nanocrystals of bioapatite, and it is not subject to remodeling during the lifetime of the individual. Mature enamel contains only 2% of proteins and bears bioapatite crystals significantly larger (up to 1000 times greater) than in bones. These differences probably reflect the adaptive capacity of vertebrates that parallels changes imposed by evolution (LeGeros and LeGeros, 1984; Mann, 2001; Skinner, 2005; Glimcher, 2006).

From the crystal-chemical point of view, apatite crystallizes in the hexagonal system and its crystallographic cell parameters, which define the geometry of the crystal lattice in three dimensions by the two parameters a (base) and c (height), vary in size in close correlation with the isomorphic iso- and hetero-valent substitutions that may occur in the various coordination sites (Hughes et al., 1989) that, additionally, impart distinctive features to bones and teeth as well. For example, there is a close correlation between the solubility of bioapatite and the partial substitution of the phosphate anion by carbonate. It is not accidental that teeth, more subject to the attack of acids, contain much less carbonate than bones in order to be less soluble. Moreover, there is an inverse proportionality ratio between concentration of carbonate and hydroxyl ions in bioapatite, as the substitution of phosphate $(\text{PO}_4)^{3-}$ with carbonate $(\text{CO}_3)^{2-}$ is counterbalanced by removal of calcium from the lattice and limiting the concentration of hydroxyl ions. As a consequence of these substitutions, the lattice is distorted and crystal growth interrupted (i.e., small sized crystals are formed). The first direct consequence is a drastic increase of the ~~surface-surface-to-to~~ surface-to-volume ratio and, thus, of the reactivity toward external molecules (Cazalbou et al., 2004; Wopenka and Pasteris, 2005; Glimcher, 2006; Boskey, 2007).

The effects of these chained events significantly affect the overall biomineralization process. Bioapatite crystal formation is, in fact, ruled by appropriate nucleation or crystallization inhibitors and crystal growth depends on the presence of biological fluids saturated with hydroxyapatite and possibly also various trace

80 elements that can be incorporated within the bioapatite frame ([Skinner, 2005](#); [Pasteris et al., 2008](#)). When
81 such inhibitors are removed, mineral growth occurs only from extracellular fluids, whose composition
82 reflects the surrounding environment. Hence several ~~researches~~studies, involving bioapatite as a biological
83 and/or environmental marker, have been carried out on fossil remains or Recent organisms (see [Keenan,](#)
84 [2016](#) for a comprehensive review).

85 This paper focuses on conodonts, ~~who~~which dominated the ancient oceans for over 300 million years
86 from the Cambrian to the Triassic. Being extinct, it is not possible to obtain reliable information about their
87 original composition and structure as the elements have undergone fossilization and diagenesis.
88 Conodonts, for a long time considered enigmatic, represent an extinct group of jawless vertebrates, that
89 were the first among the group to experiment skeletal biomineralization with tooth-like elements in their
90 feeding apparatus ([Martínez-Pérez et al., 2014](#)). These elements, ranging in average size from 0.1 to 5 mm,
91 consist of bioapatite with a francolite-like structure, and are arranged in a bilaterally-symmetrical
92 apparatus within the cephalic part of the animal. Conodonts, owing to their rapid evolution and diversity of
93 habitats, represent a fundamental biostratigraphical tool within carbonate depositional environments.
94 Moreover, as bioapatite may archive sea water chemistry information, their chemical composition
95 encourages palaeo-environmental investigations on ocean geodynamics and climates ([Holmden et al.,](#)
96 [1996](#); [Trotter et al., 1999](#); [Wenzel et al., 2000](#)).

97 In the face of these advantages offered by conodont chemical composition, it seems that fossilization
98 and diagenetic processes can affect some trace element incorporation following the biomineralization
99 process. For example, [Trotter and Eggins \(2006\)](#), through comparative analyses of contemporaneous
100 bioapatites and Holocene and Recent fish material, found a linear relationships between their respective
101 REE, Y, Pb, Th, and U incorporations, with repercussions for their possible liability to diagenesis. A similar
102 argument also applies to vertebrate enamel which, in general, is subject to isomorphic substitutions much
103 less than other mineralized vertebrate tissues ([Kohn et al., 1999](#); [Trueman and Tuross, 2002](#)).

104 Notwithstanding the numerous ~~researches~~studies that ~~accounted for take into consideration~~ trace
105 element (and isotope) incorporations in conodont bioapatite, little or nothing ~~regards~~regarding the
106 structural variations of bioapatite in conodont elements has been published. In fact it has been widely

107 demonstrated that isomorphic substitutions of major elements in apatite significantly affect the dimension
108 of cell parameters (McConnell, 1973; Hughes et al., 1989; Hughes and Rakovan, 2002; Rodríguez-Lorenzo et
109 al., 2003). Conversely, their measure can provide a nice approximation of the quantitative chemical
110 composition of major elements that, in conodonts, is not easily measurable due to their small size and a
111 lack of proper certified analytical standards with a phosphatic matrix. For example, it has been observed
112 that the cell parameter a calculated for a pure fluorapatite (obtained by synthesis) is significantly lower
113 than that of natural bioapatites which contain both hydroxyl and carbonate ions. Likewise, a progressive
114 decrease of the same cell parameter in a continuous series of crystals reflects progressive substitutions of
115 hydroxyl with fluorine (Hughes and Rakovan, 2002).

116 In this paper we measure and compare bioapatite crystallographic cell parameters in conodonts of
117 different age (Cambrian to Triassic), taxonomic assignment, geographic provenance and CAI. Furthermore,
118 cell parameters of conodont bioapatite are compared with those of coeval phosphatic or phosphatized
119 fossils ~~detected-recovered~~ from the same residue resulting from conodont preparation (i.e., brachiopods,
120 bryozoans, fish teeth, and ostracodes). The output of the comparison will be related to a possible
121 interference of fossilization and diagenesis after biomineralization. As demonstrated (Ferretti et al., 2017),
122 the calculation of the cell parameters of a single conodont element can be successfully achieved through
123 the employment of micro X-ray diffraction (μ -XRD) measurements which allow to obtain *in-situ* diffraction
124 patterns.

125

126 2. Material and methods

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128 2.1. ~~Study materials~~Material under investigation

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130 Material ~~here~~investigated herein derives from conodont collections organized at the University of
131 Modena and Reggio Emilia (IPUM Collection) in his long career by Enrico Serpagli, from material prepared
132 by one of us (AF) in her study on Late Ordovician faunas as well as from specimens kindly provided by other
133 conodont workers. A conodont assemblage of about one hundred elements (Table 1), spanning in age from

134 the Cambrian to the Triassic (Fig. 1) and including both paraconodonts and euconodonts (Fig. 2), was
135 investigated in this paper. Material results from standard conodont processing techniques.

136 In order to make comparisons between the bioapatite signal of the conodont elements and those of
137 other fossil organisms, the same analytical procedure was applied to other phosphatic/phosphatized
138 organisms selected from the same residues producing conodonts. In this way the investigation has included
139 brachiopods, bryozoans, ostracods and fish teeth (Table 2; Fig. 3).

140 All analyzed material is housed in the “Palaeontological Collections of the University of Modena and
141 Reggio Emilia: under accession prefix IPUM” at the Department of Chemical and Geological Sciences,
142 University of Modena and Reggio Emilia, Modena, Italy.

143

144 2.2 SEM/ESEM microscopy

145

146 Conodonts elements and associated phosphatic ~~associated~~ fossils were initially analyzed and
147 photographed under optical and electron microscopy. For non-conodont material, the presence of
148 bioapatite was preliminarily tested. Specimens were mounted on aluminum stubs previously covered with
149 carbon-conductive adhesive tape. Au-coated and non-coated elements were observed using an
150 Environmental Scanning Electron Microscope (ESEM) FEI ESEM-Quanta 200, equipped with an Oxford EDX
151 INCA 300 X-ray energy dispersive spectrometer and by a Scanning Electron Microscope (SEM) Nova
152 NanoSEM FEI 450 equipped with a X-EDS Bruker QUANTAX-200 detector. ESEM observations were
153 performed in high and low vacuum (low vacuum brackets 1 and 0.5 Torr) with an accelerating voltage
154 between 5 and 25 keV for imaging and between 5 and 15 keV for elemental analyses. SEM observations
155 were in high vacuum with an accelerating voltage between 15 and 25 keV for imaging and between 15 and
156 25 keV for elemental analyses.

157

158 2.3. X-ray microdiffraction (μ -XRD)

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160 X-ray diffraction measurements were carried out with a micro X-ray diffractometer. This instrument is
161 extremely versatile and allows the non-destructive study of structural properties of the material such as,
162 for example, the mineralogical composition of the crystalline phases, the degree of crystallinity, the size of
163 crystallites, the detection of preferential orientation, etc., with the same accuracy obtainable with
164 conventional diffractometers, but with the advantage of detecting measurements on very small portions of
165 the sample and, thus, on small-sized fossils. Here, μ -XRD measurements were performed on elements
166 mounted on small plane surfaces. Data were acquired using a Rigaku D/MAX RAPID diffraction system,
167 operating at 40 kV and 30 mA equipped with a CuK α source, curved-image-plate detector, flat graphite
168 monochromator, variety of beam collimators, motorized stage and microscope for accurate positioning of
169 the sample. Measurements were performed in reflection mode using a 300- μ m collimator and collection
170 times of 30 minutes and by varying the Omega and Phi angles between one sample and the other to fit with
171 the instrument geometry and thus to obtain a significant number of diffraction effects with a maximized
172 ~~signal-signal-to-to~~ noise ratio. The μ -XRD data were collected as two-dimensional images and then
173 converted into 2 θ -I profiles using the Rigaku R-Axis Display software. A 300- μ m collimator was suitable to
174 obtain mean values of bioapatite cell parameters representative of the conodont elements in their
175 wholeness.

176 Even ~~if-though~~ a previous ~~research-study~~ demonstrated that apatite overgrowth perfectly replicates the
177 original structure (Ferretti et al., 2017), when possible each point was selected ~~avoiding-to avoid~~ analyses
178 on newly formed crystals. After measurement, unit-cell parameters were refined using UnitCell software
179 (Holland and Redfern, 1997). All diffraction spots shown in the two-dimensional images were excluded ~~due~~
180 ~~to the fact that they were related because due~~ to single crystals (Ferretti et al., 2017).

181 Optical microscopy and ESEM-EDX analyses were performed at the Scientific Instruments Facility (CIGS)
182 of the University of Modena and Reggio Emilia (Modena, Italy), whereas X-ray diffraction measurements
183 were made at the Institute of Methodologies for Environmental Analysis of the National Research Council
184 of Italy of Tito Scalo (Potenza, Italy).

185

186 3. Results

187

188 3.1. Conodont faunal data

189

190 A collection of over one hundred conodont elements spanning in age from the late Cambrian to the Late
191 Triassic and including both paraconodonts and euconodonts was ~~used for our purposes~~analyzed in this
192 study. Elements were carefully selected ~~mostly and most were~~ from well-known and published sequences
193 biostratigraphically firmly constrained in order to refer to specific time-frames. Only specimens with a good
194 preservation state were analyzed. CAI covered ~~by of~~ our conodont fauna ranges from 1 to 6.

195 For a specific time frame (Late Ordovician; *Amorphognathus ordovicicus* Zone), elements occupying
196 different positions in the same apparatus were processed in order to test possible contrasting signals. Pa,
197 Pb and Sd elements of *Amorphognathus* sp., Pa and Sd elements of *Sagittodontina robusta* Knüpfer, 1967,
198 and M and Sc elements of *Hamarodus brevirameus* (Walliser, 1964) were investigated for this purpose.
199 Furthermore, results from the widely-distributed taxa *Amorphognathus* sp. and *Scabbardella altipes*
200 (Henningsmoen, 1948) were compared ~~in from~~ three geographic areas: Sardinia (Domusnovas Formation,
201 Italy; [Ferretti and Serpagli, 1999](#)) and Normandy (Vaux Limestone, France; [Ferretti et al., 2014a](#)) located
202 along the peri-Gondwana margin and Westmorland (Keisley Limestone, UK; [Bergström and Ferretti, 2015](#))
203 located in Avalonia. For a more global assessment of the Late Ordovician conodont faunas, refer to [Ferretti](#)
204 [et al. \(2014b\)](#).

205

206 3.1.1. ESEM and SEM characterization

207 Conodont elements were preliminarily investigated in order to monitor distribution of major elements.
208 Environmental scanning electron microscopy coupled with microanalyses (SEM/ESEM-EDX) was applied to
209 the entire surface of the conodont specimens, with special attention to detect variations through the
210 element wall thickness. Broken elements were carefully analyzed and scanned for this purpose. Maps of
211 major element (P, Ca, F, C, Cl, K, Na, Ba, Fe, Pb, S) distribution do not vary significantly through the element
212 wall, both for paraconodonts ([Fig. 4A](#)) and euconodonts ([Fig. 4B](#)). These findings support the presence of
213 the same carbonate-fluoroapatite in the conodont element.

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3.1.2. μ -XRD measurements and cell parameter refinements

Table SI-1 reports calculated cell parameters for conodonts (Table SI-1a) and non-conodonts (Table SI-1b) listed in Tables 1-2. If analyzed globally, our data enhance an overall considerable dispersion of the cell parameter a of the bioapatite. The cell parameter c , differently, appears to be highly variable among the euconodonts (Table S1a), and more stable in the other fossil groups, in particular paraconodonts (Table S1a) and brachiopods (Table S1b).

Selected data are plotted and discussed in the following sections.

Figure 5 plots the bioapatite crystallographic cell parameters c vs a for euconodonts and paraconodonts. It is remarkable that paraconodonts and euconodonts clearly occupy two different and ~~not non~~-overlapping fields of the plot. More in detail, the comparison clearly highlights that: i) the cell parameter a is smaller in paraconodonts than in euconodonts and it ranges between 9.337(6) and 9.392(6) (Table S1a, specimens A14 and A21, respectively); ii) values of the cell parameters c of all paraconodonts are very close to the highest values of c of the euconodonts, that ranges between 6.857(6) and 6.911(2) (Table S1a, specimens A1 and A89, respectively). Figure 6 plots the bioapatite crystallographic cell parameters c vs a for conodonts according to their age, spanning from the late Cambrian (Guzhangian) to the Late Triassic (Carnian). It is ~~well~~-highly evident that age does not affect cell parameter distribution. In fact, from a ~~close~~ chronological point of view, some values of the cell parameter a calculated for the ~~most-recent~~youngest euconodonts (Carboniferous and Triassic) are surprisingly much closer to Cambrian paraconodonts than to Ordovician euconodonts. Figure 7 plots the bioapatite crystallographic cell parameters c vs a for selected Late Ordovician conodonts according to their taxonomic assignment (Fig. 7A) and geographic area (Fig. 7B). No correlation is evident in ~~both-either~~ plots: neither taxonomy (including position occupied within the apparatus architecture) nor geographic location appear to influence cell parameter values.

3.2. Other phosphatic fauna (OPF)

240 Phosphatic/phosphatized material was picked exactly from the same residues that had produced the
241 ~~analyzed~~-conodont elements that were analyzed, in order to detect additional bioapatite signals and to
242 exclude effects of diverse preparation technique and diagenesis. Well preserved phosphatized ostracodes
243 (Fig. 3G–H, L) and undetermined material (Fig. 3F, K) were picked from the same late Cambrian residue so
244 to offer possible comparison with paraconodonts. A wider age range was covered by the analyzed
245 brachiopods (Fig. 3A–C), spanning from the Early Ordovician to the Early Devonian. Particular ~~attention~~
246 ~~effort~~ was ~~reserved-made~~ to document brachiopods from the three Late Ordovician areas (Sardinia,
247 Normandy and Westmoreland) investigated in detail also with conodonts. Only Late Ordovician bryozoans
248 (Fig. 3D–E), but from three geographic sectors, were processed for investigation. Finally, a few fish teeth
249 (Fig. 3I–J) from Upper Triassic residues were measured.
250 The presence of bioapatite was preliminarily tested by ESEM and SEM techniques so as to exclude non-
251 phosphatic material. No further chemical detailed analysis was attempted.

252

253 3.2.1. μ -XRD measurements and unit cell parameter refinements

254 **Figure 8** reports bioapatite crystallographic cell parameters for all analyzed OPF. For simplicity, the age-
255 average values of cell parameters calculated for conodonts are reported as well. Main terms of the
256 comparison are: i) values of the cell parameter *a* calculated for all the OPF are generally lower (or, at least,
257 very close) than those calculated for euconodonts, with the exception of a Late Triassic fish tooth
258 (specimen A47; Norian); ii) on the opposite, values of cell parameter *c* calculated for all the OPF are
259 significantly higher (or, at least, very close) than those calculated for euconodonts, with the exception of a
260 Late Ordovician brachiopod (specimen A55; Katian); iii) late Cambrian OPF (ostracodes and undetermined
261 material) share similar values of both cell parameters with paraconodonts, with the exception of an
262 ostracod (specimen A94; Paibian); iv) similar values were calculated also for Early Devonian (Lochkovian)
263 brachiopods and a Late Triassic (Carnian) fish tooth.

264 All results will be further discussed below. However, any conclusion from OPF should be regarded as
265 preliminary since the number of analyzed OPF specimens is significantly lower than conodonts and because

266 we could preliminar~~ily~~ly test provenance effects on cell parameters only for bryozoans and brachiopods and
267 age only for brachiopods.

268

269 4. Discussion

270

271 Bioapatites are generally classified as francolites $[\text{Ca}_5(\text{PO}_4, \text{CO}_3)_3\text{F}]$ or as dahllites $[\text{Ca}_5(\text{PO}_4, \text{CO}_3)_3(\text{OH})]$.
272 From a strict mineralogical point of view, these are no longer valid nomenclature forms (discredited by the
273 IMA in 2008) as carbonate is not the dominant species in tetrahedral isomorphic substitutions (type B
274 substitutions) (Wopenka and Pasteris, 2005). Moreover, numerous ~~researches~~ studies carried out ~~so-far-to-~~
275 date (see Liu et al., 2013 for a review) have shown that many other isomorphic substitutions occur in
276 bioapatites and, in consequence, the chemical formulas of francolite and dahllite cannot be considered
277 completely exhaustive ~~of-for~~ the composition of these biomaterials. As mentioned in the Introduction,
278 isomorphic substitutions of major elements in apatite significantly affect crystallographic cell parameter
279 dimensions. For example, substitutions of $(\text{CO}_3)^{2-}$ for $(\text{PO}_4)^{3-}$ results in an increase of the cell parameter c
280 and a contraction of the cell parameter a , whereas $(\text{CO}_3)^{2-}$ for $(\text{OH})^-$ substitution produces the opposite
281 results (LeGeros, 1981). Therefore, even if ~~to-to~~ date there is no evidence that francolite and dahllite can be
282 considered as the end-members of a continuous solid solution, it is unquestionable that the measurement
283 of cell parameters can provide a nice approximation of major element chemical composition. This approach
284 could be mandatory when both the presence of the C element and small size of the sample prevents a
285 more detailed chemical characterization than semi-quantitative EDS or EDX techniques.

286 Nemliher et al. (2004) combined X-ray diffraction on powdered sample and chemical EDX measurements
287 on fragments of Recent fish and marine mammal skeletons, phosphatic brachiopods and oceanic
288 phosphorites. Data were compared with fossil material and phosphorites of Cretaceous, Miocene and
289 Holocene age. The authors observed a reduction of the cell parameter a in fossil material and related this
290 both to the increase of carbonate content and to the decrease in the hydroxyl-ion content subsequent to
291 the recrystallization of apatite. More specifically, they proposed that the substitutions of OH with F are
292 contextual to the progressive decrease in cell volume, evidence that also suggests that these substitutions

293 do not significantly affect cell parameter *c*. Zhang et al. (2017), through a multi-analytical approach
294 combining Raman spectroscopy, high resolution X-ray diffraction and chemical analyses on well-preserved
295 Ordovician coniform conodonts from South China, documented several chemical substitutions occurring
296 during diagenesis ~~and affecting differently~~ that affect conodont tissue types (albid and hyaline crown, and
297 basal body), ~~differences differently. Such observations were~~ previously highlighted by Trotter et al. (2007)
298 in their examination of which studied hyaline and albide crown tissues using transmission electron
299 microscopy.

300 The absence of significant correlation in our euconodonts between bioapatite cell parameters and
301 taxonomic assignment, age, and geographic provenance of the elements supports the hypothesis that
302 isomorphic substitutions are not exclusively correlated with the age of the fossil. Triassic elements are, in
303 fact, much more deviated compared to the Ordovician ones (Fig. 7). On the other hand ~~opposite~~,
304 euconodont cell parameters define a higher range of values than paraconodonts (Fig. 5), even if Ordovician
305 euconodonts are closer in age to paraconodonts than to Early Triassic euconodonts. The existence of two
306 clearly separate distribution fields of cell parameters, one for paraconodonts and one for euconodonts, is
307 further strengthened plotting values of bioapatite cell volume (Fig. SI-1). Again, two distinct distributions
308 appear, one for paraconodonts and one for euconodonts. These results improve the knowledge of these
309 elements which were previously studied and distinguished using synchrotron radiation X-ray tomographic
310 microscopy to characterize and compare the microstructure of morphologically similar euconodont and
311 paraconodont elements (Murdock et al., 2013).

312 Transformation of an original bioapatite could also occur by dissolution/recrystallization processes or by
313 metasomatic substitutions. Dissolution/recrystallization drives to the formation of large-size crystals with
314 high crystallinity, whereas metasomatic substitutions normally lead to a reduction of the crystallinity and
315 do not affect crystal size. Notwithstanding ~~of which~~ between of the two ~~mentioned~~ is the main promoter of
316 the transformation, there is ~~a~~ general agreement that temperature should favor isomorphic substitution.
317 By restricting the observation to euconodonts, it was thus surprising to find no significant correlation
318 between cell parameters and CAI (Fig. SI-2). Similar conclusions are supported by Zhang et al. (2017) by the

319 analysis of conodonts exhibiting CAI of 1-3, but with no significant relationship between CAI and chemical
320 composition, Raman spectroscopic features, and crystallinity.

321 Comparison ~~between-of~~ our data and those available in similar studies on conodonts (Fig. SI-3) provides
322 a foremost endorsement of our interpretation. Unfortunately, conodont cell parameters available in the
323 literature are extremely scarce. With the exception of those reported in our previous paper (Ferretti et al.,
324 2017) and here considered, to our knowledge only two researches (Pietzner et al., 1968; Nemliher and
325 Kallaste, 2012) provide this information. Results from Pietzner et al. (1968) were not plotted as information
326 about measurements, and data management are missing. Nemliher and Kallaste (2012) applied an
327 experimental approach, different from ours, but that undoubtedly provides us ~~an~~ useful comparison tool.
328 ~~The-In fact, the~~ authors calculated ~~in-fact~~ cell parameters from X-ray spectra measured on powders
329 produced grinding various specimens of different taxa belonging to different biozones (ranging from the
330 Early Ordovician to the Silurian). Detected cell parameters could therefore be considered as an average
331 value representative of each biozone. Figure SI-3 shows that there is a nice agreement with our data,
332 including average values calculated for Ordovician elements, and those from the cited authors.

333 ~~FA-further support to-of~~ the absence of a close relationship between cell parameter values and
334 age/geographic provenance is provided by comparing signals of conodonts and other phosphatic fauna
335 (OPF) (~~Fig. 8~~). In fact, excluding the out of range cell parameter values above mentioned among OPF
336 (specimens A47 and A55), remaining data could be better sorted considering the fossil group rather than its
337 age or locality.

338 Lack of additional material does not allow ~~to-formulate~~ definitive conclusions to be formulated without
339 speculation; ~~however~~ However, if our preliminary data will-beare confirmed by further measurements on
340 larger and more varied faunal collections, including also Recent material and with diverse preservation
341 (Ferretti et al., 2012), it appears that primary biomineralization ~~appears-to-be-able-to-provides~~ an indelible
342 footprint, only mediated by fossilization and diagenetic processes.

343

344 5. Conclusions

345

346 This research has added to routine morphological and chemical qualitative characterization, achievable
347 through optical and electronic microscopy, also by integrating a crystallographic approach, based on X-ray
348 microdiffraction (μ -XRD), to gain enhanced structural information on about conodonts and other bioapatite
349 fossils. Microdiffraction measurements, recently introduced in conodont studies by our research group, is,
350 in fact, a powerful tool to for obtaining crystallographic information when dealing with small-sized samples
351 like conodont elements. Moreover, μ -XRD is a non-~~destructive~~ destructive and mandatory technique when
352 for dealing with unreplaceable-irreplaceable material. The methodological approach and the results here
353 obtained were additionally strengthened by comparison with data from the literature that had been data
354 obtained through conventional methods (X-ray powder diffraction) that parallel our findings.

355 As reported in the literature, bioapatite crystallographic cell parameters strongly depend on different
356 isomorphic substitutions. Our data reveal that cell parameters calculated for paraconodonts significantly
357 differ from those derived with for euconodonts. ~~Paraconodonts~~ In fact, paraconodonts bear ~~in fact~~ smaller
358 cell parameters a and higher cell parameters c , very close to the highest values of c of euconodonts.
359 Moreover, cell parameters calculated for both paraconodonts and euconodonts appear to be independent
360 ~~from of~~ age, taxonomic assignment, geographic provenance and, for euconodonts, CAI (i.e., temperature).
361 Other phosphatic/phosphatized material from the same residues producing conodonts are characterized by
362 values of the cell parameters that, in a preliminary way, appear to be mainly correlated with the type of
363 organism even if, for some of them, a correlation also with age cannot be completely ruled out.

364 It is, therefore, conceivable that major element content strongly depends not only on fossilization,
365 diagenesis and metasomatism, but mostly on the primary bioapatite composition. In other words, from a
366 close crystal-chemical point of view, it is not possible to unequivocally conclude, for example, that the cell
367 parameter a , smaller in paraconodonts than in euconodonts, is the direct consequence of a sort of
368 "francolization" process (i.e., the formation, for progressive and successive isomorphic substitutions, of
369 the end-member francolite that, as already pointed out, was never proved) during fossilization and/or
370 diagenesis.

371

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383

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490

491

CAPTION TO FIGURES

492

493 Fig. 1. Different time frames investigated in this ~~paper~~study plotted on the latest version of the
 494 International Commission on Stratigraphy Chronostratigraphic Chart (2018/08:
 495 <http://www.stratigraphy.org/index.php/ics-chart-timescale>; see Cohen et al., 2013, updated 2018).

496

497 Fig. 2. Some of the conodont elements analyzed in this study. A.— : *Westergaardodina* sp., late
 498 Cambrian, specimen no. A11, IPUM 29101, Västergötland (Sweden); B.— : *Furnishina alata* Szaniawski, 1971,
 499 late Cambrian, specimen no. A18, IPUM 29102, Żarnowiec (Poland); C.— : *Furnishina* sp., late Cambrian,
 500 specimen no. A14, IPUM 29103, Västergötland (Sweden); D.— : *Paltodus deltifer deltifer* (Lindström, 1955),
 501 Early Ordovician, specimen no. A6, IPUM 29104, Öland (Sweden); E.— : *Hamarodus brevirameus* (Walliser,
 502 1964), M element, Late Ordovician, specimen no. 82, IPUM 29105, Normandy (France);
 503 F.— : *Amorphognathus* sp., Pb element, Late Ordovician, specimen no. A41, IPUM 29106, Sardinia (Italy);
 504 G.— : *Amorphognathus* sp., Pb element, Late Ordovician, specimen no. A27, IPUM 29107, Westmorland (UK);

505 H-: *Lanea omoalpha* (Murphy and Valenzuela-Ríos, 1999), Early Devonian, specimen no. A2, IPUM 29108, U
 506 Topolů (Bohemia); I-: *Rhipidognathus symmetricus* Branson, Mehl and Branson, 1951, Late Ordovician,
 507 specimen no. A22, IPUM 29109, Saluda Dolomite (USA); J-: *Scabbardella altipes* (Henningsmoen, 1948),
 508 Late Ordovician, specimen no. 45, IPUM 29110, Normandy (France); K-: *Amorphognathus* sp., Pa element,
 509 Late Ordovician, specimen no. A98, IPUM 29111, Westmorland (UK); L-: *Zieglerodina planilingua* (Murphy
 510 and Valenzuela-Ríos, 1999), Early Devonian, specimen no. A1, IPUM 29112, U Topolů (Bohemia);
 511 M-: *Polygnathus decorosus* Stauffer, 1938, Late Devonian, specimen no. A83, IPUM 29113, Carnic Alps
 512 (Italy); N-: *Palmatolepis* sp., Late Devonian, specimen no. A82, IPUM 29114, Carnic Alps (Italy);
 513 O-: *Gnathodus* sp., Middle Mississippian, specimen no. A78, IPUM 29115, Carnic Alps (Italy); P-: *Branmehla*
 514 *wernerii* (Ziegler, 1957), Late Devonian, specimen no. A81, IPUM 29116, Carnic Alps (Italy); Q-: *Palmatolepis*
 515 *triangularis* Sannemann, 1955, Late Devonian, specimen no. A101, IPUM 29117, Texas (USA);
 516 R-: *Palmatolepis subperlobata* Branson and Mehl, 1934, Late Devonian, specimen no. A102, IPUM 29118,
 517 Texas (USA); S, U-: *Pachycladina obliqua* Staesche, 1964, Early Triassic, specimens no. A87 and A86, IPUM
 518 29119 and IPUM 29121, Dolomites (Italy); T-: unrecognized fragment, Early Mississippian, specimen no.
 519 A77, IPUM 29120, Carnic Alps (Italy); V-: unrecognized fragment, Middle Triassic, specimen no. A84,
 520 IPUM 29122, Dolomites (Italy); W-X-: *Carnepigondolella pseudodiebeli* (Kozur, 1972), Late Triassic,
 521 specimens no. A44 and A43, IPUM 29123 and IPUM 29124, Sicily (Italy).

522 Scale bars correspond to 200 µm.

523

524 Fig. 3. Some of the other phosphatic fauna analyzed in this study. A-C-: *Brachiopodsbrachiopods*, Early
 525 Devonian (A) and Late Ordovician (B-C), specimens no. A3, A26 and A36, IPUM 29125-29127, U Topolů
 526 (Bohemia), Westmorland (UK) and Sardinia (Italy), respectively; D-E-: *Bryozoansbryozoans*, Late
 527 Ordovician, specimens no. A24 and A61, IPUM 29128 and IPUM 29129, Saluda Dolomite (USA) and
 528 Normandy (France), respectively; F, K-: *Undetermined-undetermined* phosphatic material, late Cambrian,
 529 specimens no. A95 and A96, IPUM 29130 and IPUM 29135, Västergötland (Sweden); G-H, L-:
 530 *Ostracodesostracodes*, late Cambrian, specimens no. A17, A94 and A93, IPUM 29131, IPUM 29132 and

531 IPUM 29136, Västergötland (Sweden); I-J: ~~f~~-Fish teeth, Late Triassic, specimens no. A45 and A46, IPUM
532 29133 and IPUM 29134, Sicily (Italy).

533 Scale bars correspond to 500 μm except for G (400 μm) and H, L (300 μm).

534

535 Fig. 4. Chemical composition. ESEM image and SEM-EDS elemental maps (P, Ca, F, C, and Cl). A: ~~;~~
536 *Furnishina* sp., late Cambrian, specimen no. A110, IPUM 29137, Västergötland (Sweden). B: ~~;~~ *Scabbardella*
537 *altipes* (Henningsmoen, 1948), Late Ordovician; specimen no. A109, IPUM 29138, Normandy (France).

538 Scale bars correspond to 200 μm .

539

540 Fig. 5. Binary plot of bioapatite crystallographic unit-cell parameters c vs a for euconodonts and
541 paraconodonts.

542

543 Fig. 6. Binary plot of bioapatite crystallographic unit-cell parameters c vs a of conodonts by age.

544

545 Fig. 7. Binary plot of bioapatite crystallographic unit-cell parameters c vs a of Late Ordovician conodonts
546 by taxonomy (A) and geographic provenance (B).

547

548 Fig. 8. Binary plot of bioapatite crystallographic unit-cell parameters c vs a for other
549 phosphatic/phosphatized fauna (ostracodes, brachiopods, bryozoans and fish teeth) compared with
550 average values of conodonts by age.

551

552 CAPTION TO TABLES

553

554 Table 1. Conodont taxa analyzed in the present paper, referred to geographic location/formation, age,
555 and most relevant literature. P: paraconodont; E: euconodont.

556

557 Table 2. Other phosphatic/phosphatized taxa analyzed in the present paper, referred to geographic
558 location and age.

1 Mineralogy and crystallization patterns in conodont bioapatite from first occurrence
2 (Cambrian) to extinction (end-Triassic)

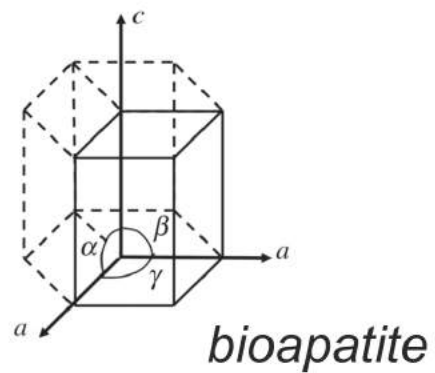
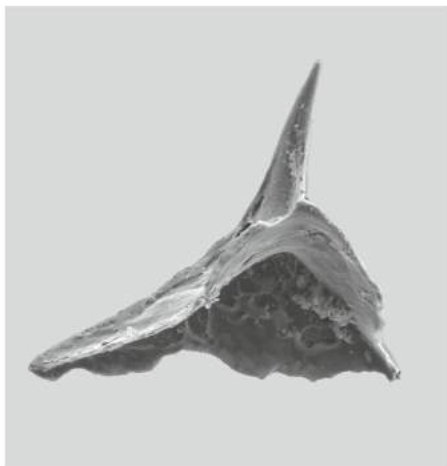
3 Luca Medici, Daniele Malferrari, Martina Savioli, Annalisa Ferretti

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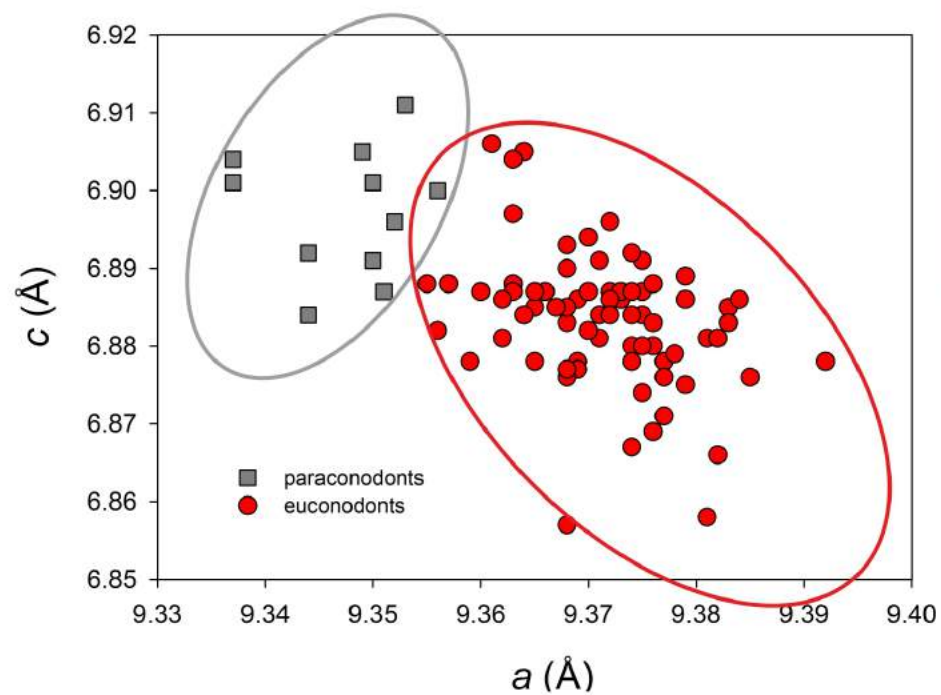
5 **Highlights**

- 6 • Bioapatite crystallographic cell parameters a and c are variable.
- 7 • Bioapatite cell parameters of paraconodonts differ from cell parameters of euconodonts.
- 8 • Age, taxonomy, geographic provenance and CAI of conodonts do not influence bioapatite cell
- 9 parameters.
- 10 • Primary bioapatite, only mediated by fossilization and diagenetic processes, rules unit cell
- 11 parameters.

PARACONODONTS



EUCONODONTS



Mineralogy and crystallization patterns in conodont bioapatite from first occurrence (Cambrian) to extinction (end-Triassic)

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ABSTRACT

Bioapatite represents an important acquisition in the evolution of life, both in the seas and on land. Vertebrates applied calcium-phosphate biominerals to grow their skeletal support and to shape their teeth, while some invertebrates sheltered their soft parts within apatite shells. Conodonts were the first among vertebrates to experiment with skeletal biomineralization of tooth-like elements in their feeding apparatus. Spanning a time record of over 300 million years, they offer a unique tool to test possible variation in bioapatite structure from the experimentation of a very primitive biomineralization type to a more evolved pattern just before going extinct. X-ray microdiffraction carried out through an X-ray micro-diffractometer, integrated with environmental scanning electron microscopy coupled with chemical microanalyses (ESEM-EDX), has been applied in this study to investigate conodont element crystal structure throughout the entire stratigraphic range of these organisms. In particular, bioapatite crystallographic cell parameters have

27 been calculated for about one hundred conodont elements ranging from the late Cambrian to the Late
28 Triassic. Resulting data clearly indicate two distinct distribution plots of cell parameters for paraconodonts
29 and euconodonts. In contrast, age, taxonomy, geographic provenance and CAI do not affect the dimension
30 of the bioapatite crystal cells. Conodont bioapatite crystallographic cell parameters have been compared
31 with cell parameters resulting from phosphatic/phosphatized material (ostracodes, brachiopods,
32 bryozoans, and fish teeth) present in the same residues producing conodonts. Resulting values of the cell
33 parameters are, in general, mainly correlated with the type of organisms even if, for some of them, a
34 correlation also with age cannot be completely ruled out. According to our data, primary bioapatite
35 appears to imprint a key signature on fossil crystal-chemistry (crystal structure and major chemical element
36 contents), while the contribution of fossilization and diagenetic processes seems less relevant.

37

38 *Keywords:* Paraconodonts; euconodonts; microdiffraction; cell parameters; biomineralization.

39

40 **1. Introduction**

41

42 Several present and fossil organisms, among both invertebrates and vertebrates, share the use of
43 bioapatite for the formation of their mineralized structures. Bioapatite has peculiar features that make it
44 suitable to act as a structural support for the body (skeleton), to allow mechanical grinding (teeth), and to
45 provide protection for the soft tissues (e.g., shell in brachiopods and skull of vertebrates) ([Kallaste and](#)
46 [Nemliher, 2005](#); [Pasteris et al., 2008](#); [Liu et al., 2013](#)). Furthermore, bioapatite is an important reserve for
47 phosphorus, a fundamental element for life that is also present in biological molecules such as DNA, RNA
48 and many proteins, and is one of the main components of ATP (adenosine triphosphate), an essential
49 molecule for the metabolism of living organisms.

50 Biomineralized structures in biological systems are made up of an organic and an inorganic component.
51 The latter is typically nanocrystalline (10^{-9} m), with nanometric assemblies of atoms with dimensions
52 ranging from ions (10^{-10} m) to macroscopic forms ([Banfield and Zhang, 2001](#)). However, there are significant
53 differences between teeth and bones. Teeth are in fact provided with cells completely different from those

involved in ossification processes, being odontoblasts specialized in the dentin formation process and ameloblasts in the formation of the enamel. Dentin consists of collagen and nanocrystals of bioapatite, and it is not subject to remodeling during the lifetime of the individual. Mature enamel contains only 2% of proteins and bears bioapatite crystals significantly larger (up to 1000 times greater) than in bones. These differences probably reflect the adaptive capacity of vertebrates that parallels changes imposed by evolution ([LeGeros and LeGeros, 1984](#); [Mann, 2001](#); [Skinner, 2005](#); [Glimcher, 2006](#)).

From the crystal-chemical point of view, apatite crystallizes in the hexagonal system and its crystallographic cell parameters, which define the geometry of the crystal lattice in three dimensions by the two parameters a (base) and c (height), vary in size in close correlation with the isomorphic iso- and hetero-valent substitutions that may occur in the various coordination sites ([Hughes et al., 1989](#)) that, additionally, impart distinctive features to bones and teeth as well. For example, there is a close correlation between the solubility of bioapatite and the partial substitution of the phosphate anion by carbonate. It is not accidental that teeth, more subject to the attack of acids, contain much less carbonate than bones in order to be less soluble. Moreover, there is an inverse proportionality ratio between concentration of carbonate and hydroxyl ions in bioapatite, as the substitution of phosphate $(\text{PO}_4)^{3-}$ with carbonate $(\text{CO}_3)^{2-}$ is counterbalanced by removal of calcium from the lattice and limiting the concentration of hydroxyl ions. As a consequence of these substitutions, the lattice is distorted and crystal growth interrupted (i.e., small sized crystals are formed). The first direct consequence is a drastic increase of the surface-to-volume ratio and, thus, of the reactivity toward external molecules ([Cazalbou et al., 2004](#); [Wopenka and Pasteris, 2005](#); [Glimcher, 2006](#); [Boskey, 2007](#)).

The effects of these chained events significantly affect the overall biomineralization process. Bioapatite crystal formation is, in fact, ruled by appropriate nucleation or crystallization inhibitors and crystal growth depends on the presence of biological fluids saturated with hydroxyapatite and possibly also various trace elements that can be incorporated within the bioapatite frame ([Skinner, 2005](#); [Pasteris et al., 2008](#)). When such inhibitors are removed, mineral growth occurs only from extracellular fluids, whose composition reflects the surrounding environment. Hence several studies, involving bioapatite as a biological and/or

80 environmental marker, have been carried out on fossil remains or Recent organisms (see [Keenan, 2016](#) for
81 a comprehensive review).

82 This paper focuses on conodonts, which dominated the ancient oceans for over 300 million years from
83 the Cambrian to the Triassic. Being extinct, it is not possible to obtain reliable information about their
84 original composition and structure as the elements have undergone fossilization and diagenesis.
85 Conodonts, for a long time considered enigmatic, represent an extinct group of jawless vertebrates, that
86 were the first among the group to experiment skeletal biomineralization with tooth-like elements in their
87 feeding apparatus ([Martínez-Pérez et al., 2014](#)). These elements, ranging in average size from 0.1 to 5 mm,
88 consist of bioapatite with a francolite-like structure, and are arranged in a bilaterally-symmetrical
89 apparatus within the cephalic part of the animal. Conodonts, owing to their rapid evolution and diversity of
90 habitats, represent a fundamental biostratigraphical tool within carbonate depositional environments.
91 Moreover, as bioapatite may archive sea water chemistry information, their chemical composition
92 encourages palaeo-environmental investigations on ocean geodynamics and climates ([Holmden et al.,](#)
93 [1996](#); [Trotter et al., 1999](#); [Wenzel et al., 2000](#)).

94 In the face of these advantages offered by conodont chemical composition, it seems that fossilization
95 and diagenetic processes can affect some trace element incorporation following the biomineralization
96 process. For example, [Trotter and Eggins \(2006\)](#), through comparative analyses of contemporaneous
97 bioapatites and Holocene and Recent fish material, found a linear relationship between their respective
98 REE, Y, Pb, Th, and U incorporations, with repercussions for their possible liability to diagenesis. A similar
99 argument also applies to vertebrate enamel which, in general, is subject to isomorphic substitutions much
100 less than other mineralized vertebrate tissues ([Kohn et al., 1999](#); [Trueman and Tuross, 2002](#)).

101 Notwithstanding the numerous studies that accounted for trace element (and isotope) incorporations in
102 conodont bioapatite, little or nothing regarding the structural variations of bioapatite in conodont elements
103 has been published. In fact it has been widely demonstrated that isomorphic substitutions of major
104 elements in apatite significantly affect the dimension of cell parameters ([McConnell, 1973](#); [Hughes et al.,](#)
105 [1989](#); [Hughes and Rakovan, 2002](#); [Rodríguez-Lorenzo et al., 2003](#)). Conversely, their measure can provide a
106 nice approximation of the quantitative chemical composition of major elements that, in conodonts, is not

107 easily measurable due to their small size and a lack of proper certified analytical standards with a
108 phosphatic matrix. For example, it has been observed that the cell parameter a calculated for a pure
109 fluorapatite (obtained by synthesis) is significantly lower than that of natural bioapatites which contain
110 both hydroxyl and carbonate ions. Likewise, a progressive decrease of the same cell parameter in a
111 continuous series of crystals reflects progressive substitutions of hydroxyl with fluorine (Hughes and
112 Rakovan, 2002).

113 In this paper we measure and compare bioapatite crystallographic cell parameters in conodonts of
114 different age (Cambrian to Triassic), taxonomic assignment, geographic provenance and CAI. Furthermore,
115 cell parameters of conodont bioapatite are compared with those of coeval phosphatic or phosphatized
116 fossils recovered from the same residue resulting from conodont preparation (i.e., brachiopods, bryozoans,
117 fish teeth, and ostracodes). The output of the comparison will be related to a possible interference of
118 fossilization and diagenesis after biomineralization. As demonstrated (Ferretti et al., 2017), the calculation
119 of the cell parameters of a single conodont element can be successfully achieved through the employment
120 of micro X-ray diffraction (μ -XRD) measurements which allow to obtain *in-situ* diffraction patterns.

121

122 2. Material and methods

123

124 2.1. Study materials

125

126 Material investigated herein derives from conodont collections organized at the University of Modena
127 and Reggio Emilia (IPUM Collection) in his long career by Enrico Serpagli, from material prepared by one of
128 us (AF) in her study on Late Ordovician faunas as well as from specimens kindly provided by other conodont
129 workers. A conodont assemblage of about one hundred elements (Table 1), spanning in age from the
130 Cambrian to the Triassic (Fig. 1) and including both paraconodonts and euconodonts (Fig. 2), was
131 investigated in this paper. Material results from standard conodont processing techniques.

132 In order to make comparisons between the bioapatite signal of the conodont elements and those of
133 other fossil organisms, the same analytical procedure was applied to other phosphatic/phosphatized

134 organisms selected from the same residues producing conodonts. In this way the investigation has included
135 brachiopods, bryozoans, ostracods and fish teeth (Table 2; Fig. 3).

136 All analyzed material is housed in the “Palaeontological Collections of the University of Modena and
137 Reggio Emilia: under accession prefix IPUM” at the Department of Chemical and Geological Sciences,
138 University of Modena and Reggio Emilia, Modena, Italy.

140 2.2 SEM/ESEM microscopy

142 Conodonts elements and associated phosphatic fossils were initially analyzed and photographed under
143 optical and electron microscopy. For non-conodont material, the presence of bioapatite was preliminarily
144 tested. Specimens were mounted on aluminum stubs previously covered with carbon-conductive adhesive
145 tape. Au-coated and non-coated elements were observed using an Environmental Scanning Electron
146 Microscope (ESEM) FEI ESEM-Quanta 200, equipped with an Oxford EDX INCA 300 X-ray energy dispersive
147 spectrometer and by a Scanning Electron Microscope (SEM) Nova NanoSEM FEI 450 equipped with a X-EDS
148 Bruker QUANTAX-200 detector. ESEM observations were performed in high and low vacuum (low vacuum
149 brackets 1 and 0.5 Torr) with an accelerating voltage between 5 and 25 keV for imaging and between 5 and
150 15 keV for elemental analyses. SEM observations were in high vacuum with an accelerating voltage
151 between 15 and 25 keV for imaging and between 15 and 25 keV for elemental analyses.

153 2.3. X-ray microdiffraction (μ -XRD)

155 X-ray diffraction measurements were carried out with a micro X-ray diffractometer. This instrument is
156 extremely versatile and allows the non-destructive study of structural properties of the material such as,
157 for example, the mineralogical composition of the crystalline phases, the degree of crystallinity, the size of
158 crystallites, the detection of preferential orientation, etc., with the same accuracy obtainable with
159 conventional diffractometers, but with the advantage of detecting measurements on very small portions of
160 the sample and, thus, on small-sized fossils. Here, μ -XRD measurements were performed on elements

161 mounted on small plane surfaces. Data were acquired using a Rigaku D/MAX RAPID diffraction system,
162 operating at 40 kV and 30 mA equipped with a CuK α source, curved-image-plate detector, flat graphite
163 monochromator, variety of beam collimators, motorized stage and microscope for accurate positioning of
164 the sample. Measurements were performed in reflection mode using a 300- μ m collimator and collection
165 times of 30 minutes and by varying the Omega and Phi angles between one sample and the other to fit with
166 the instrument geometry and thus to obtain a significant number of diffraction effects with a maximized
167 signal-to-noise ratio. The μ -XRD data were collected as two-dimensional images and then converted into
168 2 θ -I profiles using the Rigaku R-Axis Display software. A 300- μ m collimator was suitable to obtain mean
169 values of bioapatite cell parameters representative of the conodont elements in their wholeness.

170 Even though a previous study demonstrated that apatite overgrowth perfectly replicates the original
171 structure ([Ferretti et al., 2017](#)), when possible each point was selected to avoid analyses on newly formed
172 crystals. After measurement, unit-cell parameters were refined using UnitCell software ([Holland and](#)
173 [Redfern, 1997](#)). All diffraction spots shown in the two-dimensional images were excluded due to the fact
174 that they were related to single crystals ([Ferretti et al., 2017](#)).

175 Optical microscopy and ESEM-EDX analyses were performed at the Scientific Instruments Facility (CIGS)
176 of the University of Modena and Reggio Emilia (Modena, Italy), whereas X-ray diffraction measurements
177 were made at the Institute of Methodologies for Environmental Analysis of the National Research Council
178 of Italy of Tito Scalo (Potenza, Italy).

179

180 **3. Results**

181

182 *3.1. Conodont faunal data*

183

184 A collection of over one hundred conodont elements spanning in age from the late Cambrian to the Late
185 Triassic and including both paraconodonts and euconodonts was analyzed in this study. Elements were
186 carefully selected and most were from well-known and published sequences biostratigraphically firmly

187 constrained in order to refer to specific time-frames. Only specimens with a good preservation state were
188 analyzed. CAI covered of our conodont fauna ranges from 1 to 6.

189 For a specific time frame (Late Ordovician; *Amorphognathus ordovicicus* Zone), elements occupying
190 different positions in the same apparatus were processed in order to test possible contrasting signals. Pa,
191 Pb and Sd elements of *Amorphognathus* sp., Pa and Sd elements of *Sagittodontina robusta* Knüpfer, 1967,
192 and M and Sc elements of *Hamarodus brevirameus* (Walliser, 1964) were investigated for this purpose.
193 Furthermore, results from the widely-distributed taxa *Amorphognathus* sp. and *Scabbardella altipes*
194 (Henningsmoen, 1948) were compared from three geographic areas: Sardinia (Domusnovas Formation,
195 Italy; [Ferretti and Serpagli, 1999](#)) and Normandy (Vaux Limestone, France; [Ferretti et al., 2014a](#)) located
196 along the peri-Gondwana margin and Westmorland (Keisley Limestone, UK; [Bergström and Ferretti, 2015](#))
197 located in Avalonia. For a more global assessment of the Late Ordovician conodont faunas, refer to [Ferretti](#)
198 [et al. \(2014b\)](#).

199

200 3.1.1. ESEM and SEM characterization

201 Conodont elements were preliminarily investigated in order to monitor distribution of major elements.
202 Environmental scanning electron microscopy coupled with microanalyses (SEM/ESEM-EDX) was applied to
203 the entire surface of the conodont specimens, with special attention to detect variations through the
204 element wall thickness. Broken elements were carefully analyzed and scanned for this purpose. Maps of
205 major element (P, Ca, F, C, Cl, K, Na, Ba, Fe, Pb, S) distribution do not vary significantly through the element
206 wall, both for paraconodonts ([Fig. 4A](#)) and euconodonts ([Fig. 4B](#)). These findings support the presence of
207 the same carbonate-fluoroapatite in the conodont element.

208

209 3.1.2. μ -XRD measurements and cell parameter refinements

210 [Table SI-1](#) reports calculated cell parameters for conodonts ([Table SI-1a](#)) and non-conodonts ([Table SI-](#)
211 [1b](#)) listed in [Tables 1-2](#). If analyzed globally, our data enhance an overall considerable dispersion of the cell
212 parameter *a* of the bioapatite. The cell parameter *c*, differently, appears to be highly variable among the

213 euconodonts (Table S1a), and more stable in the other fossil groups, in particular paraconodonts (Table
214 S1a) and brachiopods (Table S1b). Selected data are plotted and discussed in the following sections.

215 Figure 5 plots the bioapatite crystallographic cell parameters c vs a for euconodonts and paraconodonts.
216 It is remarkable that paraconodonts and euconodonts clearly occupy two different and non-overlapping
217 fields of the plot. More in detail, the comparison clearly highlights that: i) the cell parameter a is smaller in
218 paraconodonts than in euconodonts and it ranges between 9.337(6) and 9.392(6) (Table S1a, specimens
219 A14 and A21, respectively); ii) values of the cell parameter c of all paraconodonts are very close to the
220 highest values of c of the euconodonts that ranges between 6.857(6) and 6.911(2) (Table S1a, specimens
221 A1 and A89, respectively). Figure 6 plots the bioapatite crystallographic cell parameters c vs a for
222 conodonts according to their age, spanning from the late Cambrian (Guzhangian) to the Late Triassic
223 (Carnian). It is highly evident that age does not affect cell parameter distribution. In fact, from a
224 chronological point of view, some values of the cell parameter a calculated for the youngest euconodonts
225 (Carboniferous and Triassic) are surprisingly much closer to Cambrian paraconodonts than to Ordovician
226 euconodonts. Figure 7 plots the bioapatite crystallographic cell parameters c vs a for selected Late
227 Ordovician conodonts according to their taxonomic assignment (Fig. 7A) and geographic area (Fig. 7B). No
228 correlation is evident in either plots: neither taxonomy (including position occupied within the apparatus
229 architecture) nor geographic location appear to influence cell parameter values.

230

231 3.2. Other phosphatic fauna (OPF)

232

233 Phosphatic/phosphatized material was picked exactly from the same residues that had produced the
234 conodont elements that were analyzed, in order to detect additional bioapatite signals and to exclude
235 effects of diverse preparation technique and diagenesis. Well preserved phosphatized ostracodes (Fig. 3G–
236 H, L) and undetermined material (Fig. 3F, K) were picked from the same late Cambrian residue so to offer
237 possible comparison with paraconodonts. A wider age range was covered by the analyzed brachiopods (Fig.
238 3A–C), spanning from the Early Ordovician to the Early Devonian. Particular effort was made to document
239 brachiopods from the three Late Ordovician areas (Sardinia, Normandy and Westmoreland) investigated in

240 detail also with conodonts. Only Late Ordovician bryozoans (Fig. 3D–E), but from three geographic sectors,
241 were processed for investigation. Finally, a few fish teeth (Fig. 3I–J) from Upper Triassic residues were
242 measured. The presence of bioapatite was preliminarily tested by ESEM and SEM techniques so as to
243 exclude non-phosphatic material. No further chemical detailed analysis was attempted.

244

245 3.2.1. μ -XRD measurements and unit cell parameter refinements

246 Figure 8 reports bioapatite crystallographic cell parameters for all analyzed OPF. For simplicity, the age-
247 average values of cell parameters calculated for conodonts are reported as well. Main terms of the
248 comparison are: i) values of the cell parameter a calculated for all the OPF are generally lower (or, at least,
249 very close) than those calculated for euconodonts, with the exception of a Late Triassic fish tooth
250 (specimen A47; Norian); ii) on the opposite, values of cell parameter c calculated for all the OPF are
251 significantly higher (or, at least, very close) than those calculated for euconodonts, with the exception of a
252 Late Ordovician brachiopod (specimen A55; Katian); iii) late Cambrian OPF (ostracodes and undetermined
253 material) share similar values of both cell parameters with paraconodonts, with the exception of an
254 ostracod (specimen A94; Paibian); iv) similar values were calculated also for Early Devonian (Lochkovian)
255 brachiopods and a Late Triassic (Carnian) fish tooth.

256 All results will be further discussed below. However, any conclusion from OPF should be regarded as
257 preliminary since the number of analyzed OPF specimens is significantly lower than conodonts and because
258 we could preliminarily test provenance effects on cell parameters only for bryozoans and brachiopods and
259 age only for brachiopods.

260

261 4. Discussion

262

263 Bioapatites are generally classified as francolites [$\text{Ca}_5(\text{PO}_4, \text{CO}_3)_3\text{F}$] or as dahllites [$\text{Ca}_5(\text{PO}_4, \text{CO}_3)_3(\text{OH})$].
264 From a strict mineralogical point of view, these are no longer valid nomenclature forms (discredited by the
265 IMA in 2008) as carbonate is not the dominant species in tetrahedral isomorphic substitutions (type B
266 substitutions) (Wopenka and Pasteris, 2005). Moreover, numerous studies carried out to-date (see Liu et

267 [al., 2013](#) for a review) have shown that many other isomorphic substitutions occur in bioapatites and, in
268 consequence, the chemical formulas of francolite and dahllite cannot be considered completely exhaustive
269 for the composition of these biomaterials. As mentioned in the Introduction, isomorphic substitutions of
270 major elements in apatite significantly affect crystallographic cell parameter dimensions. For example,
271 substitutions of $(\text{CO}_3)^{2-}$ for $(\text{PO}_4)^{3-}$ results in an increase of the cell parameter c and a contraction of the cell
272 parameter a , whereas $(\text{CO}_3)^{2-}$ for $(\text{OH})^-$ substitution produces the opposite results ([LeGeros, 1981](#)).
273 Therefore, even if to-date there is no evidence that francolite and dahllite can be considered as the end-
274 members of a continuous solid solution, it is unquestionable that the measurement of cell parameters can
275 provide a nice approximation of major element chemical composition. This approach could be mandatory
276 when both the presence of the C element and small size of the sample prevents a more detailed chemical
277 characterization than semi-quantitative EDS or EDX techniques.

278 [Nemliher et al. \(2004\)](#) combined X-ray diffraction on powdered sample and chemical EDX measurements
279 on fragments of Recent fish and marine mammal skeletons, phosphatic brachiopods and oceanic
280 phosphorites. Data were compared with fossil material and phosphorites of Cretaceous, Miocene and
281 Holocene age. The authors observed a reduction of the cell parameter a in fossil material and related this
282 both to the increase of carbonate content and to the decrease in the hydroxyl-ion content subsequent to
283 the recrystallization of apatite. More specifically, they proposed that the substitutions of OH with F are
284 contextual to the progressive decrease in cell volume, evidence that also suggests that these substitutions
285 do not significantly affect cell parameter c . [Zhang et al. \(2017\)](#), through a multi-analytical approach
286 combining Raman spectroscopy, high resolution X-ray diffraction and chemical analyses on well-preserved
287 Ordovician coniform conodonts from South China, documented several chemical substitutions occurring
288 during diagenesis that affect conodont tissue types (albid and hyaline crown, and basal body) differently.
289 Such observations were previously highlighted by Trotter et al. (2007) in their examination of hyaline and
290 albid crown tissues using transmission electron microscopy.

291 The absence of significant correlation in our euconodonts between bioapatite cell parameters and
292 taxonomic assignment, age, and geographic provenance of the elements supports the hypothesis that
293 isomorphic substitutions are not exclusively correlated with the age of the fossil. Triassic elements are, in

294 fact, much more deviated compared to the Ordovician ones (Fig. 7). On the other hand, euconodont cell
295 parameters define a higher range of values than paraconodonts (Fig. 5), even if Ordovician euconodonts
296 are closer in age to paraconodonts than to Early Triassic euconodonts. The existence of two clearly
297 separate distribution fields of cell parameters, one for paraconodonts and one for euconodonts, is further
298 strengthened plotting values of bioapatite cell volume (Fig. SI-1). Again, two distinct distributions appear,
299 one for paraconodonts and one for euconodonts. These results improve the knowledge of these elements
300 which were previously studied and distinguished using synchrotron radiation X-ray tomographic microscopy
301 to characterize and compare the microstructure of morphologically similar euconodont and paraconodont
302 elements (Murdock et al., 2013).

303 Transformation of an original bioapatite could also occur by dissolution/recrystallization processes or by
304 metasomatic substitutions. Dissolution/recrystallization drives to the formation of large-size crystals with
305 high crystallinity, whereas metasomatic substitutions normally lead to a reduction of the crystallinity and
306 do not affect crystal size. Notwithstanding which of the two is the main promoter of the transformation,
307 there is general agreement that temperature should favor isomorphic substitution. By restricting the
308 observation to euconodonts, it was thus surprising to find no significant correlation between cell
309 parameters and CAI (Fig. SI-2). Similar conclusions are supported by Zhang et al. (2017) by the analysis of
310 conodonts exhibiting CAI of 1-3, but with no significant relationship between CAI and chemical
311 composition, Raman spectroscopic features, and crystallinity.

312 Comparison of our data and those available in similar studies on conodonts (Fig. SI-3) provides a
313 foremost endorsement of our interpretation. Unfortunately, conodont cell parameters available in the
314 literature are extremely scarce. With the exception of those reported in our previous paper (Ferretti et al.,
315 2017) and here considered, to our knowledge only two researches (Pietzner et al., 1968; Nemliher and
316 Kallaste, 2012) provide this information. Results from Pietzner et al. (1968) were not plotted as information
317 about measurements, and data management are missing. Nemliher and Kallaste (2012) applied an
318 experimental approach, different from ours, but that undoubtedly provides us a useful comparison tool. In
319 fact, the authors calculated cell parameters from X-ray spectra measured on powders produced grinding
320 various specimens of different taxa belonging to different biozones (ranging from the Early Ordovician to

321 the Silurian). Detected cell parameters could therefore be considered as an average value representative of
322 each biozone. [Figure SI-3](#) shows that there is a nice agreement with our data, including average values
323 calculated for Ordovician elements, and those from the cited authors.

324 Further support of the absence of a close relationship between cell parameter values and
325 age/geographic provenance is provided by comparing signals of conodonts and other phosphatic fauna
326 (OPF) ([Fig. 8](#)). In fact, excluding the out of range cell parameter values above mentioned among OPF
327 (specimens A47 and A55), remaining data could be better sorted considering the fossil group rather than its
328 age or locality.

329 Lack of additional material does not allow definitive conclusions to be formulated without speculation.
330 However, if our preliminary data are confirmed by further measurements on larger and more varied faunal
331 collections, including also Recent material and with diverse preservation ([Ferretti et al., 2012](#)), it appears
332 that primary biomineralization provides an indelible footprint, only mediated by fossilization and diagenetic
333 processes.

335 5. Conclusions

337 This research has added to routine morphological and chemical qualitative characterization, achievable
338 through optical and electronic microscopy, by integrating a crystallographic approach based on X-ray
339 microdiffraction (μ -XRD) to gain enhanced structural information about conodonts and other bioapatite
340 fossils. Microdiffraction measurements, recently introduced in conodont studies by our research group, is,
341 in fact, a powerful tool for obtaining crystallographic information when dealing with small-sized samples
342 like conodont elements. Moreover, μ -XRD is a non-destructive technique for dealing with irreplaceable
343 material. The methodological approach and the results here obtained were additionally strengthened by
344 comparison with data from the literature that had been obtained through conventional methods (X-ray
345 powder diffraction) that parallel our findings.

346 As reported in the literature, bioapatite crystallographic cell parameters strongly depend on different
347 isomorphic substitutions. Our data reveal that cell parameters calculated for paraconodonts significantly

348 differ from those derived for euconodonts. In fact, paraconodonts bear smaller cell parameters a and
349 higher cell parameters c , very close to the highest values of c of euconodonts. Moreover, cell parameters
350 calculated for both paraconodonts and euconodonts appear to be independent of age, taxonomic
351 assignment, geographic provenance and, for euconodonts, CAI (i.e., temperature). Other
352 phosphatic/phosphatized material from the same residues producing conodonts are characterized by
353 values of the cell parameters that, in a preliminary way, appear to be mainly correlated with the type of
354 organism even if, for some of them, a correlation also with age cannot be completely ruled out.

355 It is, therefore, conceivable that major element content strongly depends not only on fossilization,
356 diagenesis and metasomatism, but mostly on the primary bioapatite composition. In other words, from a
357 close crystal-chemical point of view, it is not possible to unequivocally conclude, for example, that the cell
358 parameter a , smaller in paraconodonts than in euconodonts, is the direct consequence of a sort of
359 "francolization" process (i.e., the formation, for progressive and successive isomorphic substitutions, of
360 the end-member francolite that, as already pointed out, was never proved) during fossilization and/or
361 diagenesis.

362

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374

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481

482

CAPTION TO FIGURES

483

484 Fig. 1. Different time frames investigated in this study plotted on the latest version of the International
485 Commission on Stratigraphy Chronostratigraphic Chart (2018/08:
486 <http://www.stratigraphy.org/index.php/ics-chart-timescale>; see Cohen et al., 2013, updated 2018).

487

488 Fig. 2. Some of the conodont elements analyzed in this study. A: *Westergaardodina* sp., late Cambrian,
489 specimen no. A11, IPUM 29101, Västergötland (Sweden); B: *Furnishina alata* Szaniawski, 1971, late
490 Cambrian, specimen no. A18, IPUM 29102, Żarnowiec (Poland); C: *Furnishina* sp., late Cambrian, specimen
491 no. A14, IPUM 29103, Västergötland (Sweden); D: *Paltodus deltifer deltifer* (Lindström, 1955), Early
492 Ordovician, specimen no. A6, IPUM 29104, Öland (Sweden); E: *Hamarodus brevirameus* (Walliser, 1964), M
493 element, Late Ordovician, specimen no. 82, IPUM 29105, Normandy (France); F: *Amorphognathus* sp., Pb
494 element, Late Ordovician, specimen no. A41, IPUM 29106, Sardinia (Italy); G: *Amorphognathus* sp., Pb
495 element, Late Ordovician, specimen no. A27, IPUM 29107, Westmorland (UK); H: *Lanea omoalpha* (Murphy
496 and Valenzuela-Ríos, 1999), Early Devonian, specimen no. A2, IPUM 29108, U Topolů (Bohemia);
497 I: *Rhipidognathus symmetricus* Branson, Mehl and Branson, 1951, Late Ordovician, specimen no. A22, IPUM
498 29109, Saluda Dolomite (USA); J: *Scabbardella altipes* (Henningsmoen, 1948), Late Ordovician, specimen
499 no. 45, IPUM 29110, Normandy (France); K: *Amorphognathus* sp., Pa element, Late Ordovician, specimen
500 no. A98, IPUM 29111, Westmorland (UK); L: *Zieglerodina planilingua* (Murphy and Valenzuela-Ríos, 1999),
501 Early Devonian, specimen no. A1, IPUM 29112, U Topolů (Bohemia); M: *Polygnathus decorosus* Stauffer,
502 1938, Late Devonian, specimen no. A83, IPUM 29113, Carnic Alps (Italy); N: *Palmatolepis* sp., Late
503 Devonian, specimen no. A82, IPUM 29114, Carnic Alps (Italy); O: *Gnathodus* sp., Middle Mississippian,
504 specimen no. A78, IPUM 29115, Carnic Alps (Italy); P: *Branmehla wernerii* (Ziegler, 1957), Late Devonian,

specimen no. A81, IPUM 29116, Carnic Alps (Italy); Q: *Palmatolepis triangularis* Sannemann, 1955, Late Devonian, specimen no. A101, IPUM 29117, Texas (USA); R: *Palmatolepis subperlobata* Branson and Mehl, 1934, Late Devonian, specimen no. A102, IPUM 29118, Texas (USA); S, U: *Pachycladina obliqua* Staesche, 1964, Early Triassic, specimens no. A87 and A86, IPUM 29119 and IPUM 29121, Dolomites (Italy); T: unrecognizable fragment, Early Mississippian, specimen no. A77, IPUM 29120, Carnic Alps (Italy); V: unrecognizable fragment, Middle Triassic, specimen no. A84, IPUM 29122, Dolomites (Italy); W-X: *Carnepigondolella pseudodiebeli* (Kozur, 1972), Late Triassic, specimens no. A44 and A43, IPUM 29123 and IPUM 29124, Sicily (Italy).

Scale bars correspond to 200 μm .

Fig. 3. Some of the other phosphatic fauna analyzed in this study. A-C: brachiopods, Early Devonian (A) and Late Ordovician (B-C), specimens no. A3, A26 and A36, IPUM 29125-29127, U Topolů (Bohemia), Westmorland (UK) and Sardinia (Italy), respectively; D-E: bryozoans, Late Ordovician, specimens no. A24 and A61, IPUM 29128 and IPUM 29129, Saluda Dolomite (USA) and Normandy (France), respectively; F, K: undetermined phosphatic material, late Cambrian, specimens no. A95 and A96, IPUM 29130 and IPUM 29135, Västergötland (Sweden); G-H, L: ostracodes, late Cambrian, specimens no. A17, A94 and A93, IPUM 29131, IPUM 29132 and IPUM 29136, Västergötland (Sweden); I-J: fish teeth, Late Triassic, specimens no. A45 and A46, IPUM 29133 and IPUM 29134, Sicily (Italy).

Scale bars correspond to 500 μm except for G (400 μm) and H, L (300 μm).

Fig. 4. Chemical composition. ESEM image and SEM-EDS elemental maps (P, Ca, F, C, and Cl). A: *Furnishina* sp., late Cambrian, specimen no. A110, IPUM 29137, Västergötland (Sweden). B: *Scabbardella altipes* (Henningsmoen, 1948), Late Ordovician; specimen no. A109, IPUM 29138, Normandy (France).

Scale bars correspond to 200 μm .

Fig. 5. Binary plot of bioapatite crystallographic unit-cell parameters c vs a for euconodonts and paraconodonts.

532

533 Fig. 6. Binary plot of bioapatite crystallographic unit-cell parameters c vs a of conodonts by age.

534

535 Fig. 7. Binary plot of bioapatite crystallographic unit-cell parameters c vs a of Late Ordovician conodonts
536 by taxonomy (A) and geographic provenance (B).

537

538 Fig. 8. Binary plot of bioapatite crystallographic unit-cell parameters c vs a for other
539 phosphatic/phosphatized fauna (ostracodes, brachiopods, bryozoans and fish teeth) compared with
540 average values of conodonts by age.

541

542 CAPTION TO TABLES

543

544 Table 1. Conodont taxa analyzed in the present paper, referred to geographic location/formation, age,
545 and most relevant literature. P: paraconodont; E: euconodont.

546

547 Table 2. Other phosphatic/phosphatized taxa analyzed in the present paper, referred to geographic
548 location and age.



INTERNATIONAL CHRONOSTRATIGRAPHIC CHART




























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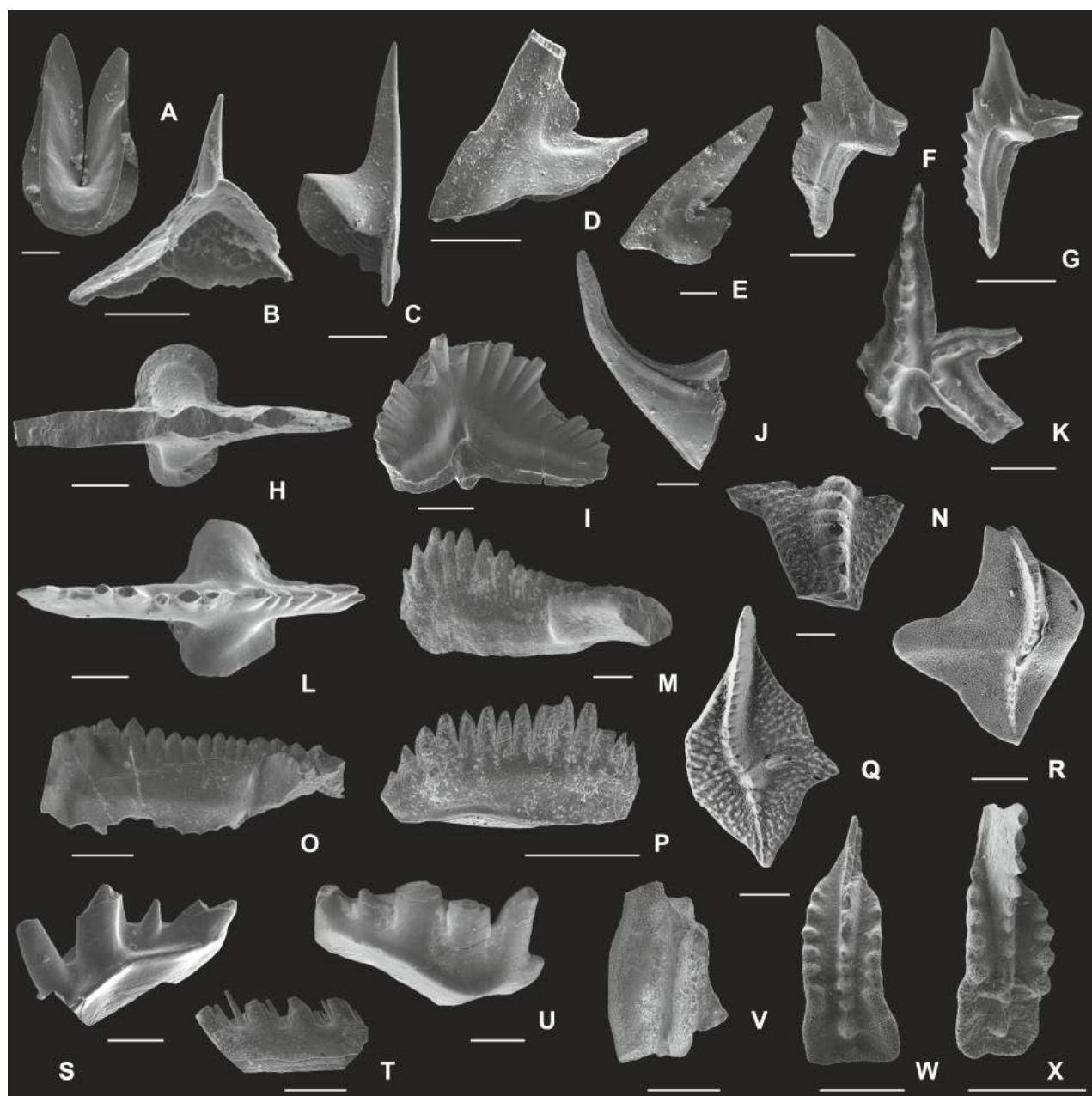
International Commission on Stratigraphy

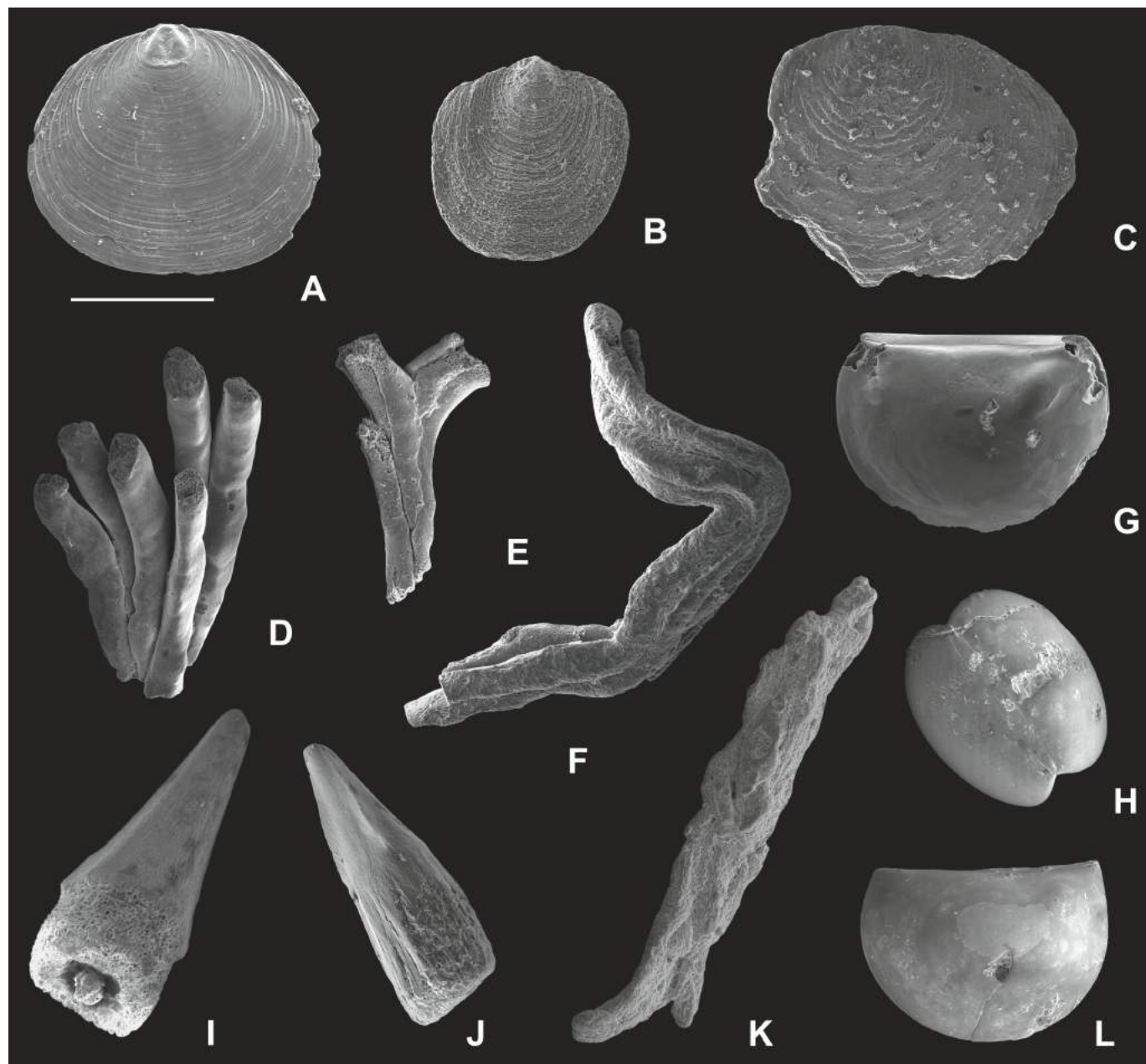
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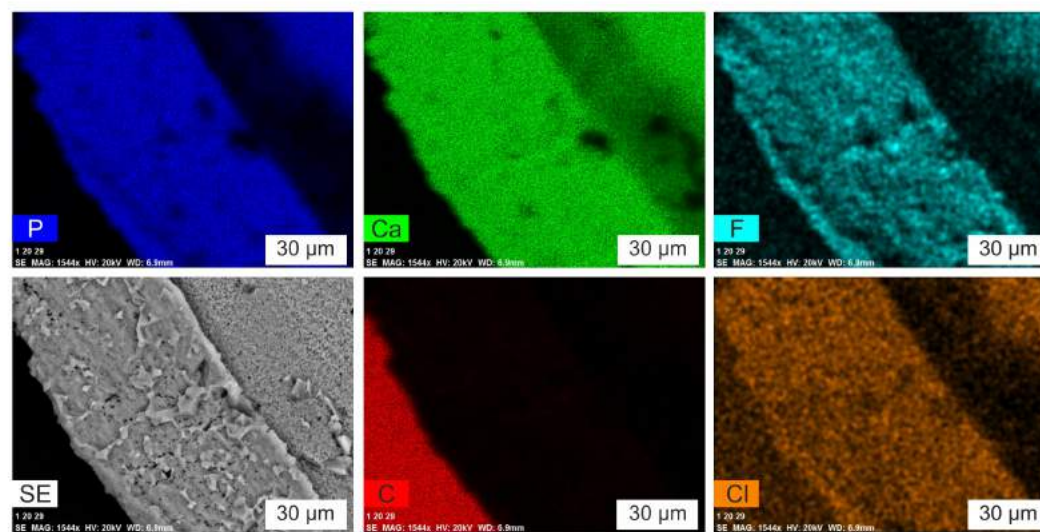
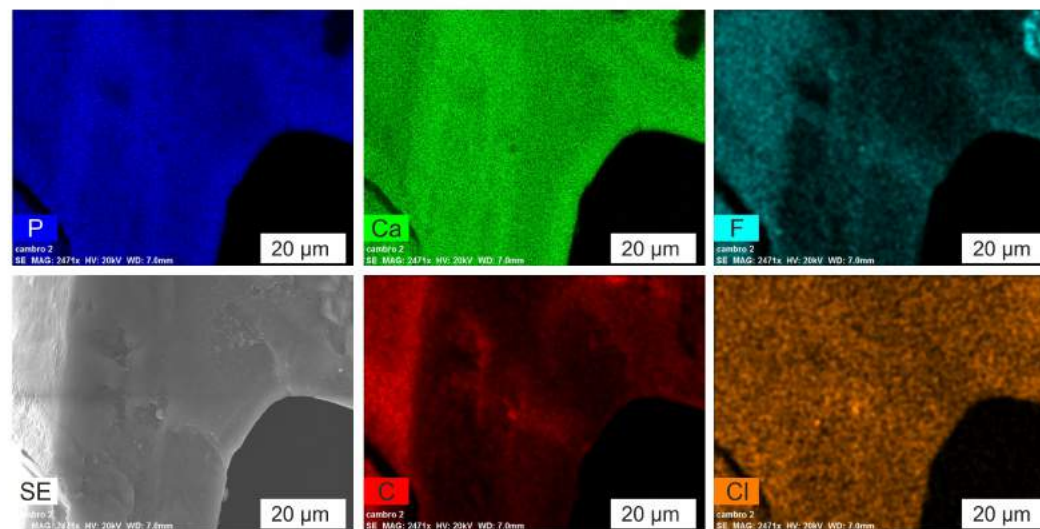
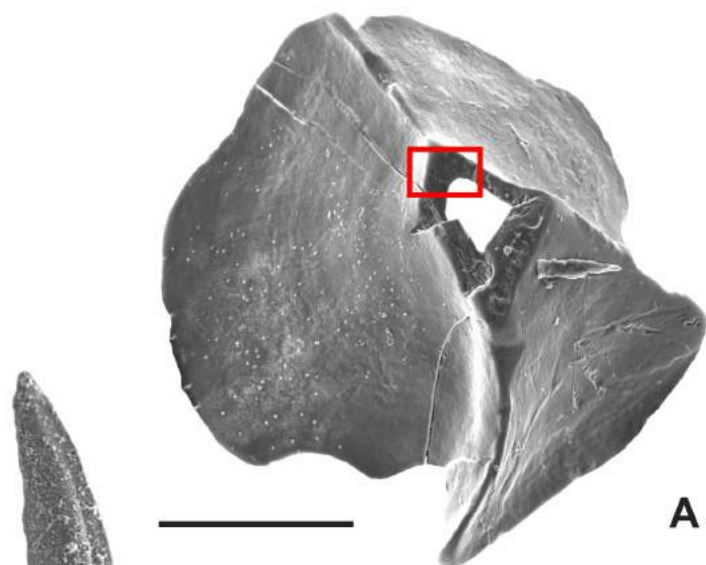


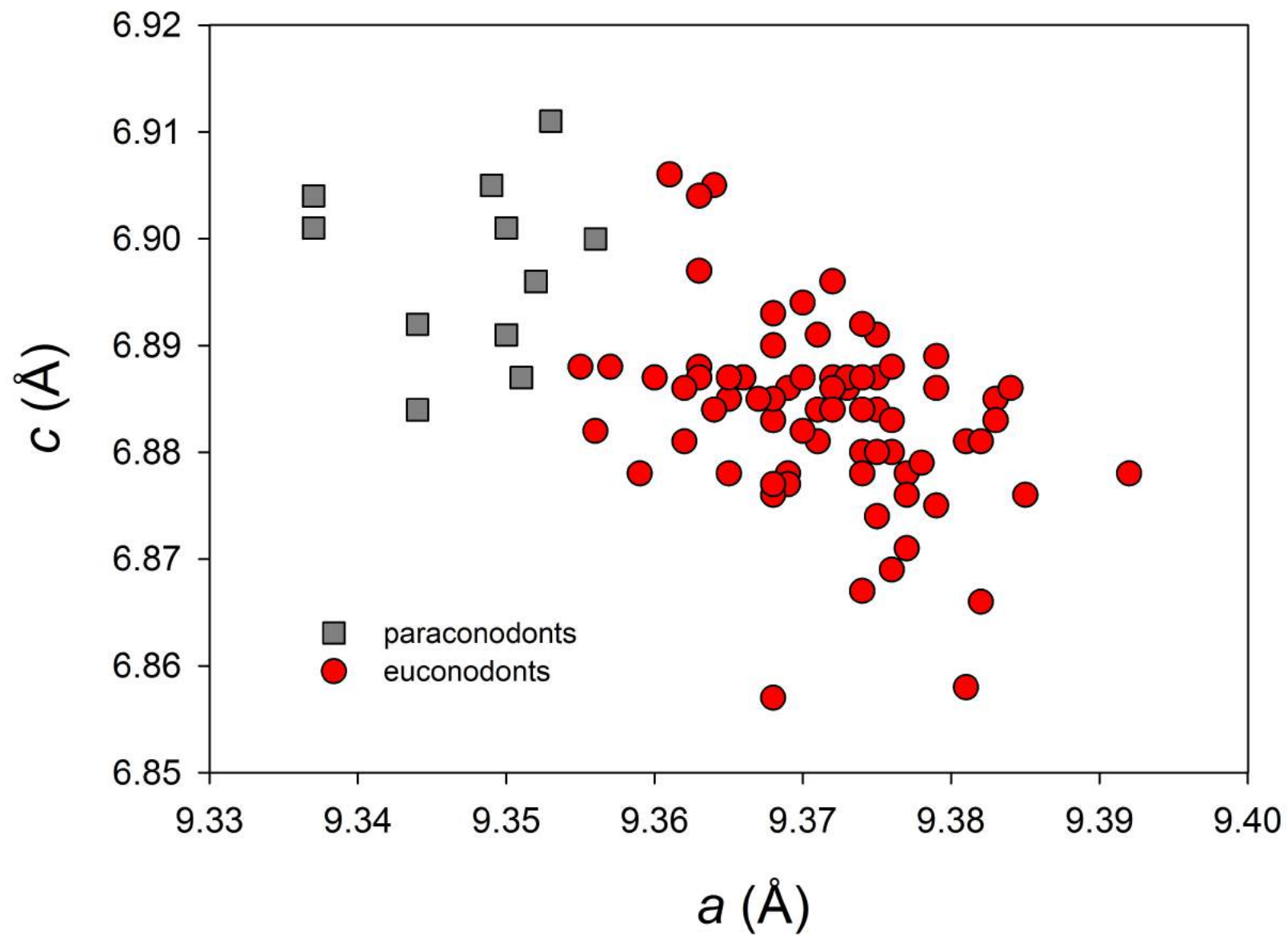
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Phanerozoic	Mesozoic	Triassic	Upper				Rhaetian	
							Norian	
							Carnian	★
			Middle				Ladinian	★
							Anisian	★
							Olenekian	★
							Induan	★
	Paleozoic	Permian	Lopingian				Changhsingian	★
							Wuchiapingian	★
			Guadalupian				Capitanian	★
							Wordian	★
							Roadian	★
			Cisuralian				Kungurian	
							Artinskian	
							Sakmarian	★
							Asselian	★
		Pennsylvanian	Upper				Gzhelian	
							Kasimovian	
			Middle				Moscovian	
	Carboniferous	Mississippian	Lower				Bashkirian	★
			Upper				Serpukhovian	
			Middle				Visean	★
			Lower				Tournaisian	★

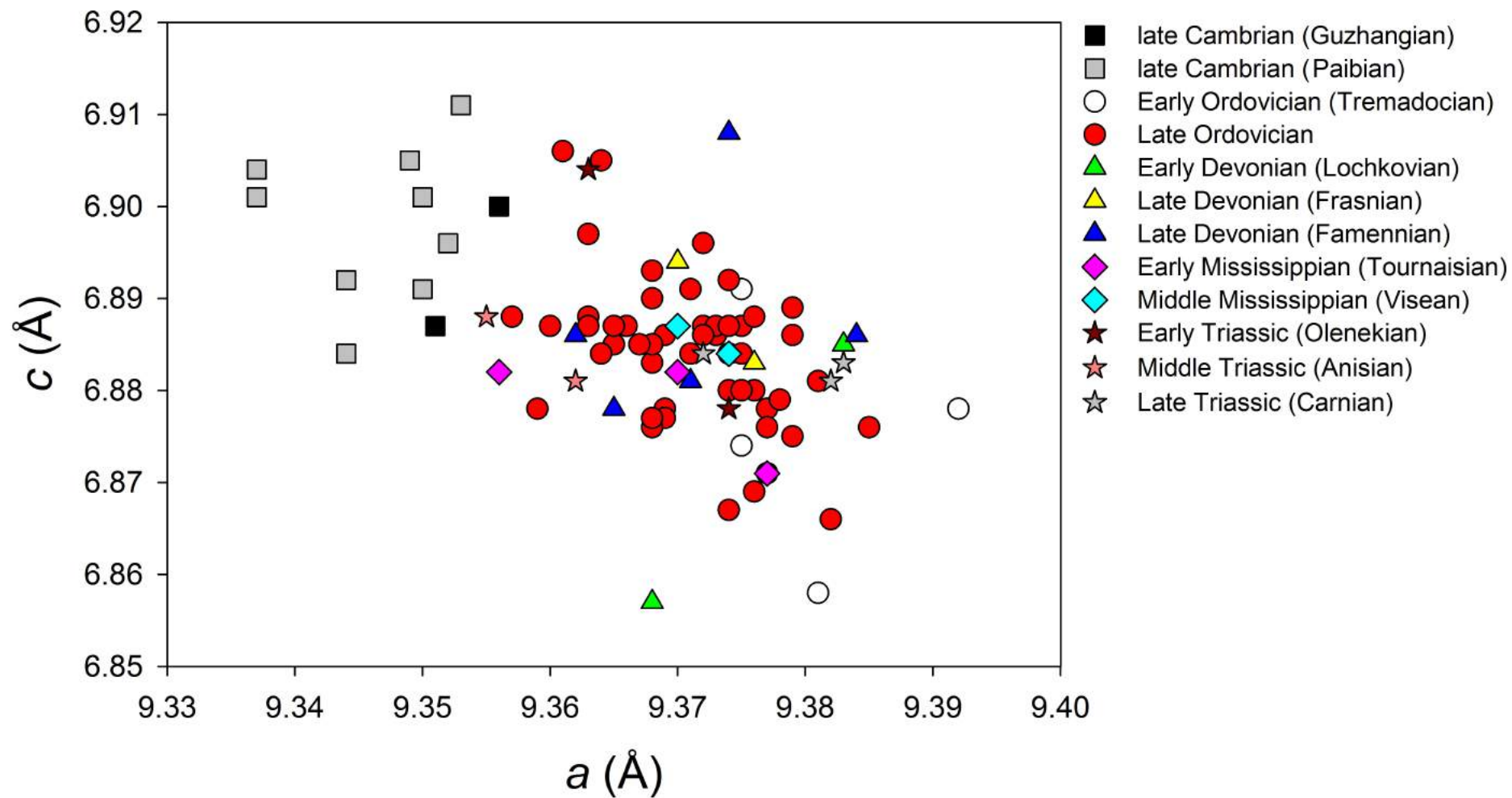
Eonothem / Eon		Erathem / Era		System / Period		Series / Epoch	Stage / Age	GSSP
Phanerozoic	Paleozoic	Devonian	Upper	Famennian				
				Frasnian				
			Middle	Givetian				
				Eifelian				
			Lower	Emsian				
				Pragian				
				Lochkovian				
		Silurian	Pridoli					
			Ludlow	Ludfordian				
				Gorstian				
			Wenlock	Homerian				
				Sheinwoodian				
			Llandovery	Telychian				
				Aeronian				
		Rhuddanian						
		Ordovician	Upper	Hirnantian				
				Katian				
			Middle	Sandbian				
				Darriwilian				
			Lower	Dapingian				
				Floian				
				Tremadocian				
		Cambrian	Furongian	Stage 10				
				Jiangshanian				
				Paibian				
			Miaolingian	Guzhangian				
				Drumian				
				Wuliuan				
			Series 2	Stage 4				
				Stage 3				
			Terreneuvian	Stage 2				
		Fortunian						

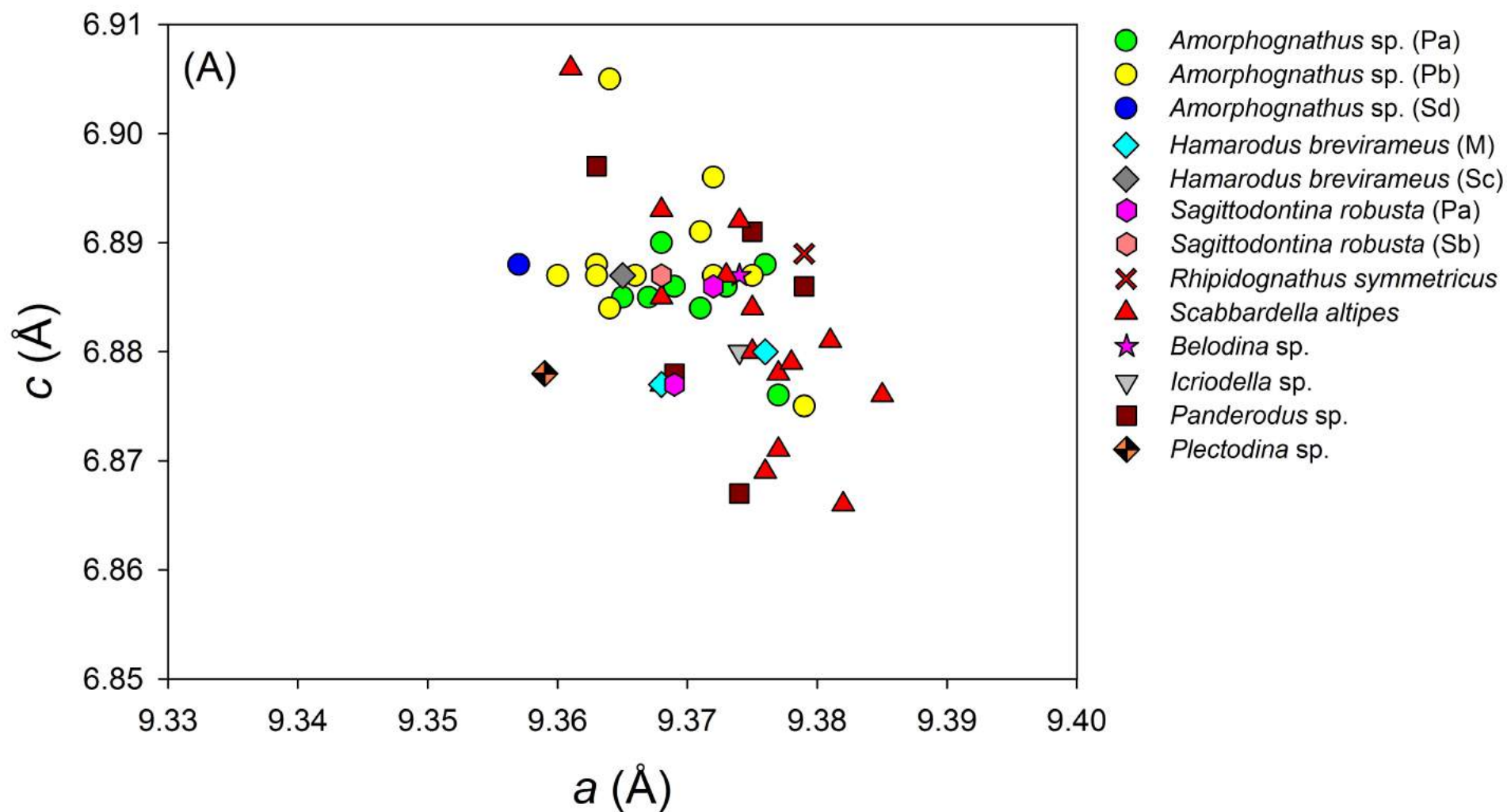


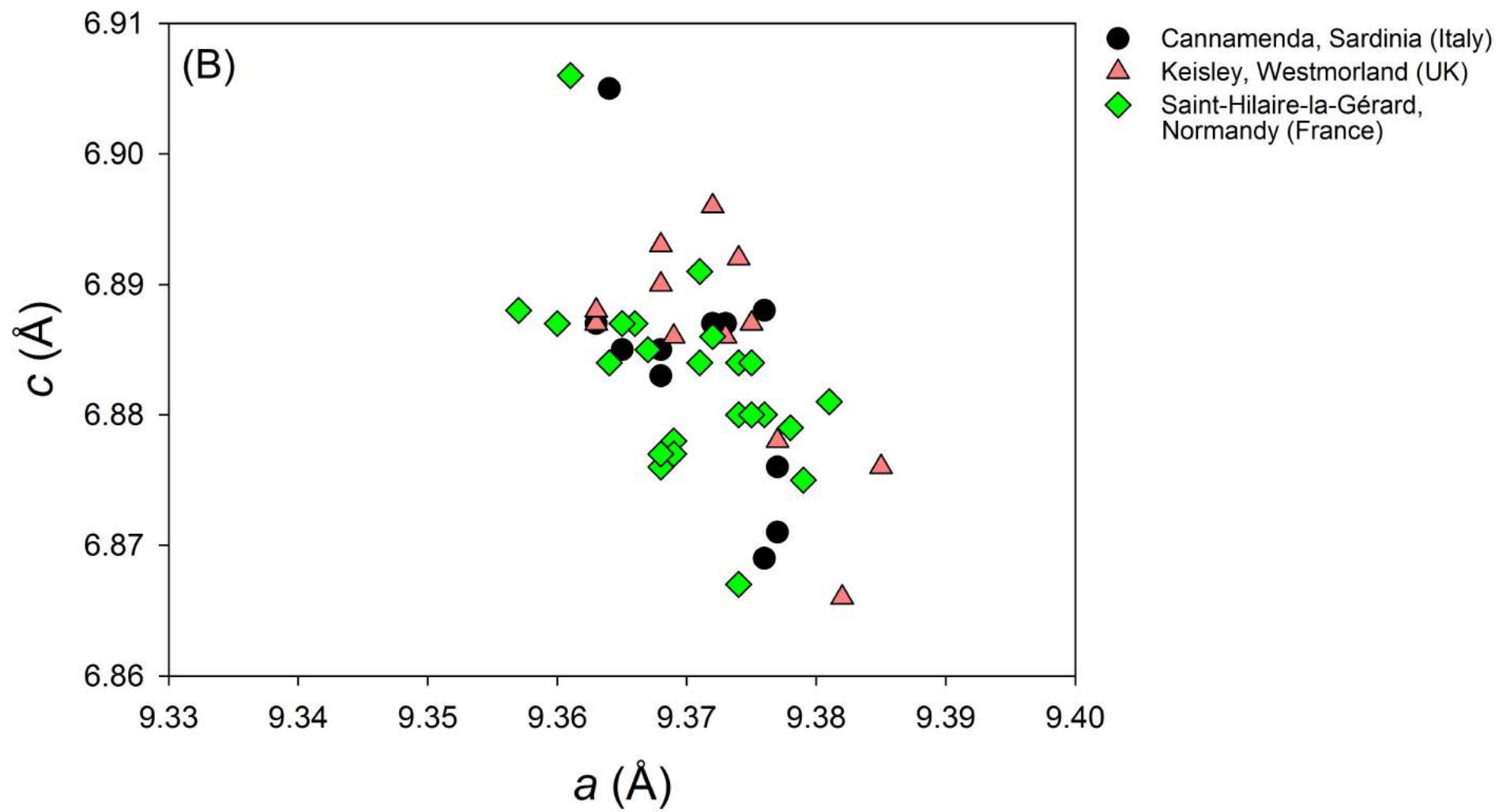


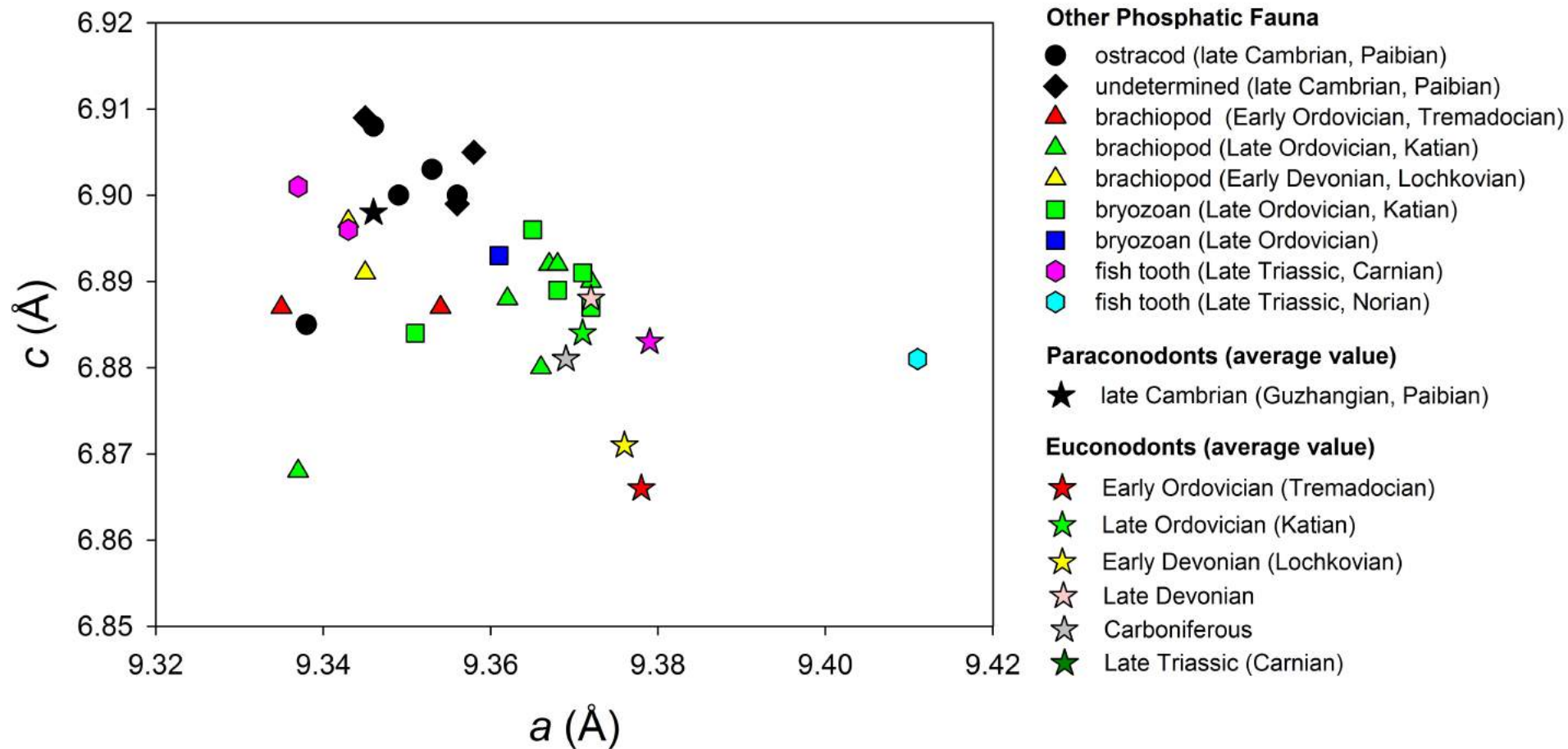












Code	n° elements	Conodont taxa	Locality/Formation	Age	P/E	CAI	reference paper(s)/ collection
A18-A19	2	<i>Furnishina alata</i> Szaniawski, 1971	Żarnowiec (Poland)	Cambrian Miaolingian (Guzhangian)	P		Szaniawski, 1971
A11-A12, A90-A91	4	<i>Westergaardodina</i> sp.	Kinneulle, Västergötland (Sweden)	Cambrian Furongian (Paibian)	P		Müller and Hinz, 1991
A13-A14, A88-A89, A110	4	<i>Furnishina</i> sp.	Kinneulle, Västergötland (Sweden)	Cambrian Furongian (Paibian)	P		Müller and Hinz, 1991
A15	1	unrecognizable fragment	Kinneulle, Västergötland (Sweden)	Cambrian Furongian (Paibian)	P		Müller and Hinz, 1991
A5-A6	2	<i>Paltodus deltifer deltifer</i> (Lindström, 1955)	Öland (Sweden)	Early Ordovician (Tremadocian)	E	1.5	IPUM Collection
A10	1	unrecognizable fragment	Öland (Sweden)	Early Ordovician (Tremadocian)	E	1.5	IPUM Collection
A20-A21	2	<i>Paltodus deltifer pristinus</i> (Viira, 1970)	Northern Estonia	Early Ordovician (Tremadocian)	E	1.5	Viira, 1970
A30-A31, A98-A99	4	<i>Amorphognathus</i> sp. (Pa)	Keisley, Westmorland (UK)	Late Ordovician (Katian)	E	4	Bergström and Ferretti, 2015
A27-A29	3	<i>Amorphognathus</i> sp. (Pb)	Keisley, Westmorland (UK)	Late Ordovician (Katian)	E	4	Bergström and Ferretti, 2015
A32-A34, A74-A75	5	<i>Scabbardella altipes</i> (Henningsmoen, 1948)	Keisley, Westmorland (UK)	Late Ordovician (Katian)	E	4	Bergström and Ferretti, 2015
A38, A66-A67	3	<i>Amorphognathus</i> sp. (Pa)	Cannamenda, Sardinia (Italy)	Late Ordovician (Katian)	E	5	Ferretti and Serpagli, 1999
A37, A41, A68, A72	4	<i>Amorphognathus</i> sp. (Pb)	Cannamenda, Sardinia (Italy)	Late Ordovician (Katian)	E	5	Ferretti and Serpagli, 1999
A39-A40, A69-A70	4	<i>Scabbardella altipes</i> (Henningsmoen, 1948)	Cannamenda, Sardinia (Italy)	Late Ordovician (Katian)	E	5	Ferretti and Serpagli, 1999
A49-A51	3	<i>Amorphognathus</i> sp. (Pa)	Saint-Hilaire-la-Gérard, Normandy (France)	Late Ordovician (Katian)	E	4-5	Ferretti et al., 2014a
62, A52, A107-A108	4	<i>Amorphognathus</i> sp. (Pb)	Saint-Hilaire-la-Gérard, Normandy (France)	Late Ordovician (Katian)	E	4-5	Ferretti et al., 2014a
17	1	<i>Amorphognathus</i> sp. (Sd)	Saint-Hilaire-la-Gérard,	Late Ordovician (Katian)	E	4-5	Ferretti et al., 2014a

			Normandy (France)				
68, 82	2	<i>Hamarodus brevirameus</i> (Walliser, 1964) (M)	Saint-Hilaire-la-Gérard, Normandy (France)	Late Ordovician (Katian)	E	4-5	Ferretti et al., 2014a
49	1	<i>Hamarodus brevirameus</i> (Walliser, 1964) (Sc)	Saint-Hilaire-la-Gérard, Normandy (France)	Late Ordovician (Katian)	E	4-5	Ferretti et al., 2014a
21	1	<i>Icriodella</i> sp.	Saint-Hilaire-la-Gérard, Normandy (France)	Late Ordovician (Katian)	E	4-5	Ferretti et al., 2014a
20, 56, A53	3	<i>Panderodus</i> sp.	Saint-Hilaire-la-Gérard, Normandy (France)	Late Ordovician (Katian)	E	4-5	Ferretti et al., 2014a
24, 41	2	<i>Sagittodontina robusta</i> Knüpfer, 1967 (Pa)	Saint-Hilaire-la-Gérard, Normandy (France)	Late Ordovician (Katian)	E	4-5	Ferretti et al., 2014a
46	1	<i>Sagittodontina robusta</i> Knüpfer, 1967 (Sd)	Saint-Hilaire-la-Gérard, Normandy (France)	Late Ordovician (Katian)	E	4-5	Ferretti et al., 2014a
45, 59-60, 91, 103, A54, A109	6	<i>Scabbardella altipes</i> (Henningsmoen, 1948)	Saint-Hilaire-la-Gérard, Normandy (France)	Late Ordovician (Katian)	E	4-5	Ferretti et al., 2014a
A22	1	<i>Rhipidognathus symmetricus</i> Branson, Mehl and Branson, 1951	Saluda Dolomite (USA)	Late Ordovician	E	1	IPUM Collection
A23	1	<i>Panderodus</i> sp.	Saluda Dolomite (USA)	Late Ordovician	E	1	IPUM Collection
A104	1	<i>Belodina</i> sp.	Kimmswick Formation, Missouri (USA)	Late Ordovician	E	1	IPUM Collection
A105	1	<i>Plectodina</i> sp.	Kimmswick Formation, Missouri (USA)	Late Ordovician	E	1	IPUM Collection
A106	1	<i>Panderodus</i> sp.	Kimmswick Formation, Missouri (USA)	Late Ordovician	E	1	IPUM Collection
A1	1	<i>Zieglerodina planilingua</i> (Murphy and Valenzuela-Ríos, 1999)	U Topolů (Bohemia)	Early Devonian (Lochkovian)	E	3	Chlupáč et al., 1980
A2	1	<i>Lanea omoalpha</i> (Murphy and Valenzuela- Ríos, 1999)	U Topolů (Bohemia)	Early Devonian (Lochkovian)	E	3	Chlupáč et al., 1980
A82	1	<i>Palmatolepis</i> sp.	Pramosio A, Carnic Alps (Italy)	Late Devonian (Frasnian)	E	4.5	Spalletta and Perri, 1998a
A83	1	<i>Polygnathus decorosus</i> Stauffer, 1938	Pramosio A, Carnic Alps (Italy)	Late Devonian (Frasnian)	E	4.5	Spalletta and Perri, 1998a
A80	1	unrecognizable fragment	Casera Collinetta di Sotto A, Carnic Alps (Italy)	Late Devonian (Famennian)	E	4.5	Perri and Spalletta, 1998

A81	1	<i>Branmehla weneri</i> (Ziegler, 1957)	Casera Collinetta di Sotto A, Carnic Alps (Italy)	Late Devonian (Famennian)	E	4.5	Perri and Spalletta, 1998
A101	1	<i>Palmatolepis triangularis</i> Sannemann, 1955	Texas (USA)	Late Devonian (Famennian)	E	2	IPUM Collection
A102	1	<i>Palmatolepis subperlobata</i> Branson and Mehl, 1934	Texas (USA)	Late Devonian (Famennian)	E	2	IPUM Collection
A103	1	<i>Icriodus</i> sp.	Texas (USA)	Late Devonian (Famennian)	E	2	IPUM Collection
A76-A77, A100	3	unrecognizable fragments	Dolina, Carnic Alps (Italy)	Carboniferous Early Mississippian (Tournaisian)	E	4.5	Spalletta and Perri, 1998b
A78-A79	2	<i>Gnathodus</i> sp.	Dolina, Carnic Alps (Italy)	Carboniferous Middle Mississippian (Viséan)	E	4-4.5	Spalletta and Perri, 1998b
A86-A87	2	<i>Pachycladina obliqua</i> Staesche, 1964	Cencenighe Galleria, Dolomites (Italy)	Early Triassic (Olenekian)	E	5.5-6	Perri and Andraghetti, 1987
A84-A85	2	unrecognizable fragments	Sotto le Rive, Dolomites (Italy)	Middle Triassic (Anisian)	E	1.5	Kovačs et al., 1996; Farabegoli and Perri, 1998
A42-A44	3	<i>Carnepigondolella pseudodiebeli</i> (Kozur, 1972)	Pizzo Mondello, Sicani Mountains, Sicily (Italy)	Late Triassic (Carnian)	E	1.5	Mazza et al., 2012; Mazza and Martínez-Pérez, 2015

Code	Faunal element	Locality	Age
A16	ostracod	Kinneulle, Västergötland (Sweden)	Cambrian Furongian (Paibian)
A17	ostracod	Kinneulle, Västergötland (Sweden)	Cambrian Furongian (Paibian)
A92	ostracod	Kinneulle, Västergötland (Sweden)	Cambrian Furongian (Paibian)
A93	ostracod	Kinneulle, Västergötland (Sweden)	Cambrian Furongian (Paibian)
A94	ostracod	Kinneulle, Västergötland (Sweden)	Cambrian Furongian (Paibian)
A95	undetermined	Kinneulle, Västergötland (Sweden)	Cambrian Furongian (Paibian)
A96	undetermined	Kinneulle, Västergötland (Sweden)	Cambrian Furongian (Paibian)
A97	undetermined	Kinneulle, Västergötland (Sweden)	Cambrian Furongian (Paibian)
A7	brachiopod	Öland (Sweden)	Early Ordovician (Tremadocian)
A8	brachiopod	Öland (Sweden)	Early Ordovician (Tremadocian)
A9	brachiopod	Öland (Sweden)	Early Ordovician (Tremadocian)
A25	brachiopod	Keisley, Westmorland (UK)	Late Ordovician (Katian)
A26	brachiopod	Keisley, Westmorland (UK)	Late Ordovician (Katian)
A73	brachiopod	Cannamenda, Sardinia (Italy)	Late Ordovician (Katian)
A36	brachiopod	Cannamenda, Sardinia (Italy)	Late Ordovician (Katian)
A55	brachiopod	Saint-Hilaire-la-Gérard, Normandy (France)	Late Ordovician (Katian)
A64	brachiopod	Saint-Hilaire-la-Gérard, Normandy (France)	Late Ordovician (Katian)
A3	brachiopod	U Topolů (Bohemia)	Early Devonian (Lochkovian)
A4	brachiopod	U Topolů (Bohemia)	Early Devonian (Lochkovian)
A35	bryozoan	Cannamenda, Sardinia (Italy)	Late Ordovician (Katian)
A71	bryozoan	Cannamenda, Sardinia (Italy)	Late Ordovician (Katian)
A58	bryozoan	Saint-Hilaire-la-Gérard, Normandy (France)	Late Ordovician (Katian)
A61	bryozoan	Saint-Hilaire-la-Gérard, Normandy (France)	Late Ordovician (Katian)
A65	bryozoan	Saint-Hilaire-la-Gérard, Normandy (France)	Late Ordovician (Katian)
A24	bryozoan	Saluda Dolomite (USA)	Late Ordovician
A45	fish tooth	Pizzo Mondello, Sicani Mountains, Sicily (Italy)	Late Triassic (Carnian)
A46	fish tooth	Pizzo Mondello, Sicani Mountains, Sicily (Italy)	Late Triassic (Carnian)
A47	fish tooth	Pizzo Mondello, Sicani Mountains, Sicily (Italy)	Late Triassic (Norian)

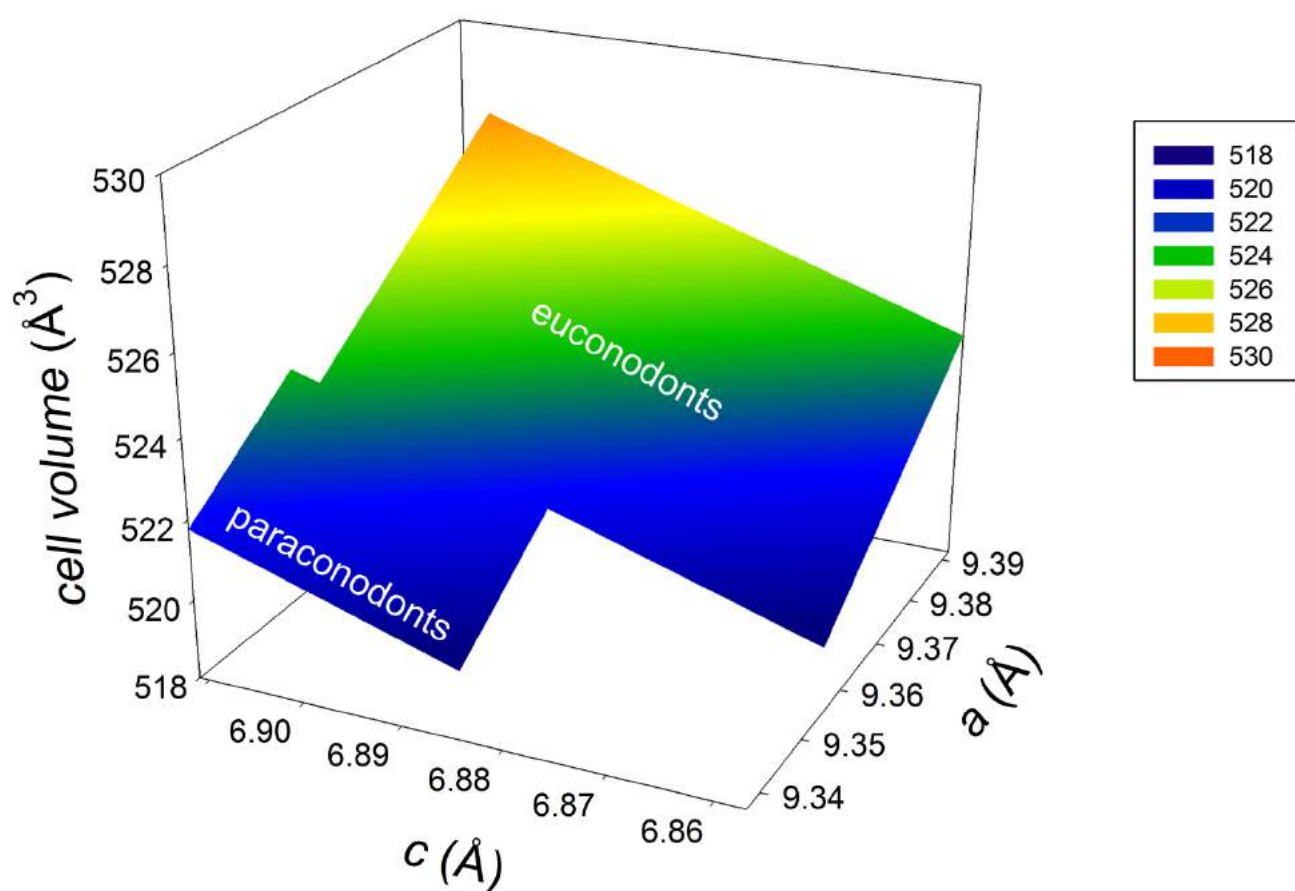


Figure SI-1. Bioapatite cell volume distribution surface calculated for paraconodonts and euconodonts.

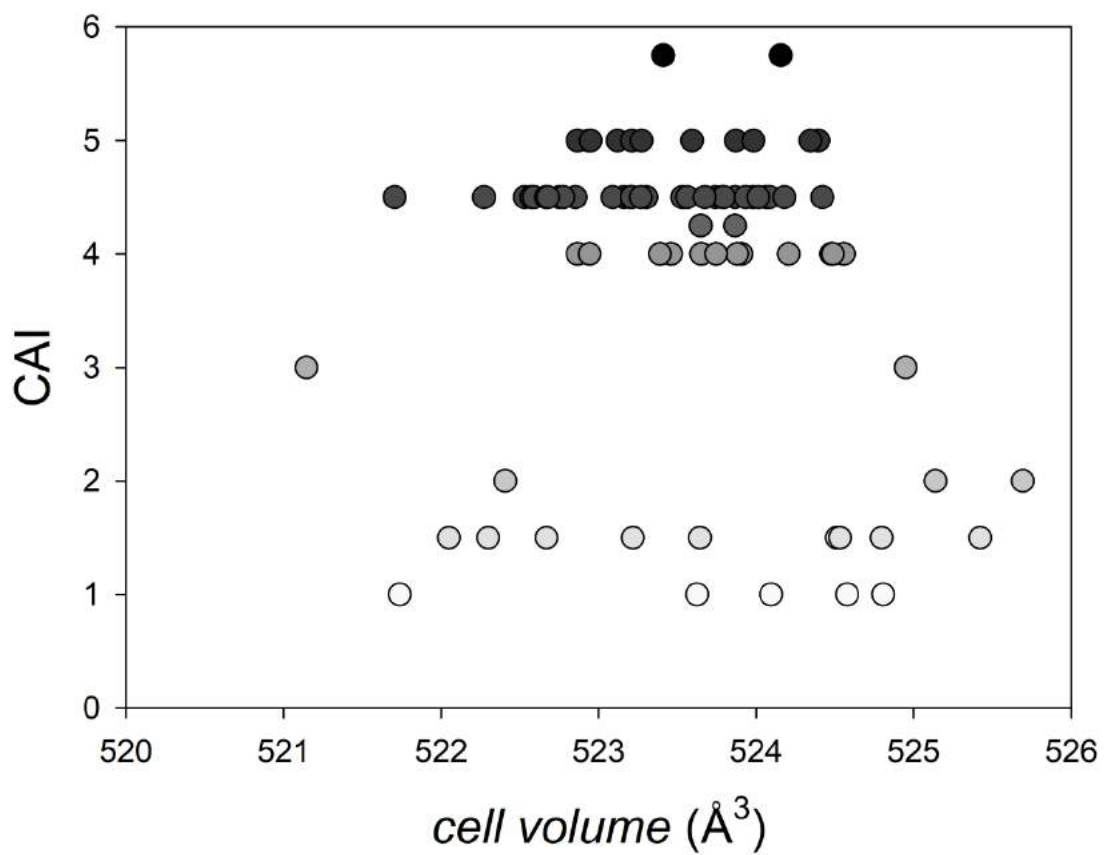


Figure SI-2. Distribution of bioapatite cell volumes calculated for euconodonts in function of the CAI. Grey tones are used exclusively to facilitate reading (light grey, low CAI; dark grey, high CAI).

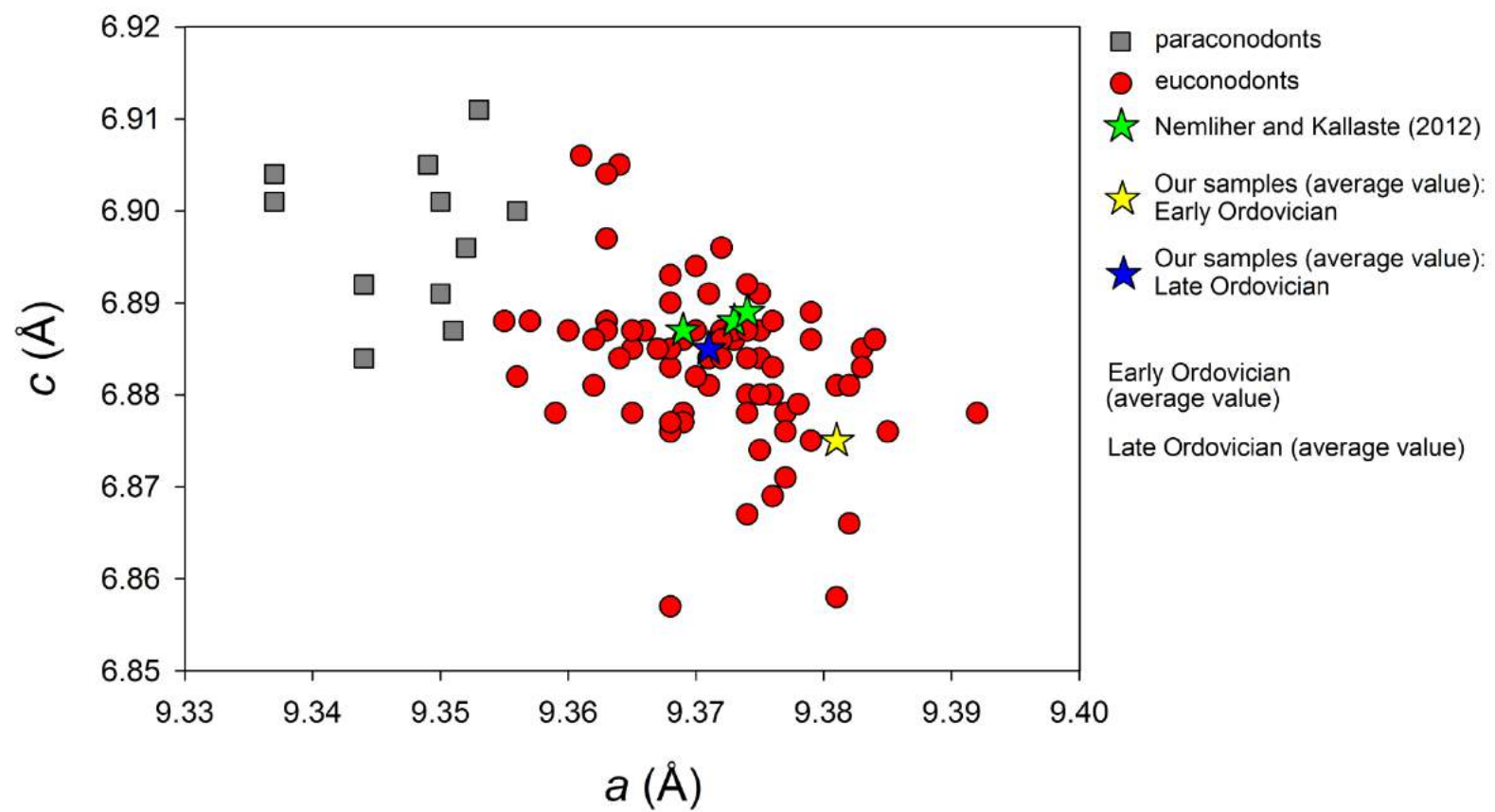


Figure SI-3. Binary plot of bioapatite unit-cell parameters c vs a for our euconodonts and paraconodonts compared with literature data.

Table SI-1a. Bioapatite cell parameters calculated for conodonts. For additional details, see Table 1. P: paraconodont; E: euconodont.

Code	<i>a</i> (Å)	<i>c</i> (Å)	Taxa	Locality/Formation	Age	P / E	CAI
A18	9.356(6)	6.900(4)	<i>Furnishina alata</i> Szaniawski, 1971	Żarnowiec (Poland)	Cambrian Miaolingian (Guzhangian)	P	
A19	9.351(4)	6.887(4)	<i>Furnishina alata</i> Szaniawski, 1971	Żarnowiec (Poland)	Cambrian Miaolingian (Guzhangian)	P	
A11	9.344(4)	6.892(4)	<i>Westergaardodina</i> sp.	Kinne-kulle, Västergötland (Sweden)	Cambrian Furongian (Paibian)	P	
A12	9.344(3)	6.884(3)	<i>Westergaardodina</i> sp.	Kinne-kulle, Västergötland (Sweden)	Cambrian Furongian (Paibian)	P	
A90	9.350(4)	6.891(3)	<i>Westergaardodina</i> sp.	Kinne-kulle, Västergötland (Sweden)	Cambrian Furongian (Paibian)	P	
A91	9.352(4)	6.896(4)	<i>Westergaardodina</i> sp.	Kinne-kulle, Västergötland (Sweden)	Cambrian Furongian (Paibian)	P	
A13	9.349(2)	6.905(2)	<i>Furnishina</i> sp.	Kinne-kulle, Västergötland (Sweden)	Cambrian Furongian (Paibian)	P	
A14	9.337(6)	6.901(5)	<i>Furnishina</i> sp.	Kinne-kulle, Västergötland (Sweden)	Cambrian Furongian (Paibian)	P	
A88	9.350(3)	6.901(5)	<i>Furnishina</i> sp.	Kinne-kulle, Västergötland (Sweden)	Cambrian Furongian (Paibian)	P	
A89	9.353(2)	6.911(2)	<i>Furnishina</i> sp.	Kinne-kulle, Västergötland (Sweden)	Cambrian Furongian (Paibian)	P	
A15	9.337(3)	6.904(2)	unrecognizable fragment	Kinne-kulle, Västergötland (Sweden)	Cambrian Furongian (Paibian)	P	
A5	9.375(3)	6.874(5)	<i>Paltodus deltifer deltifer</i> (Lindström, 1955)	Öland (Sweden)	Early Ordovician (Tremadocian)	E	1.5
A6	9.381(2)	6.858(6)	<i>Paltodus deltifer deltifer</i> (Lindström, 1955)	Öland (Sweden)	Early Ordovician (Tremadocian)	E	1.5

A20	9.375(2)	6.891(4)	<i>Paltodus deltifer deltifer</i> (Lindström, 1955)	Northern Estonia	Early Ordovician (Tremadocian)	E	1.5
A21	9.392(6)	6.878(6)	<i>Paltodus deltifer deltifer</i> (Lindström, 1955)	Northern Estonia	Early Ordovician (Tremadocian)	E	1.5
A30	9.363(2)	6.887(3)	<i>Amorphognathus</i> sp. (Pa)	Keisley, Westmorland (UK)	Late Ordovician (Katian)	E	4
A31	9.368(5)	6.890(3)	<i>Amorphognathus</i> sp. (Pa)	Keisley, Westmorland (UK)	Late Ordovician (Katian)	E	4
A98	9.369(2)	6.886(4)	<i>Amorphognathus</i> sp. (Pa)	Keisley, Westmorland (UK)	Late Ordovician (Katian)	E	4
A99	9.373(3)	6.886(4)	<i>Amorphognathus</i> sp. (Pa)	Keisley, Westmorland (UK)	Late Ordovician (Katian)	E	4
A27	9.375(2)	6.887(3)	<i>Amorphognathus</i> sp. (Pb)	Keisley, Westmorland (UK)	Late Ordovician (Katian)	E	4
A28	9.372(2)	6.896(2)	<i>Amorphognathus</i> sp. (Pb)	Keisley, Westmorland (UK)	Late Ordovician (Katian)	E	4
A29	9.363(3)	6.888(6)	<i>Amorphognathus</i> sp. (Pb)	Keisley, Westmorland (UK)	Late Ordovician (Katian)	E	4
A32	9.382(3)	6.866(6)	<i>Scabbardella altipes</i> (Henningsmoen, 1948)	Keisley, Westmorland (UK)	Late Ordovician (Katian)	E	4
A33	9.374(3)	6.892(5)	<i>Scabbardella altipes</i> (Henningsmoen, 1948)	Keisley, Westmorland (UK)	Late Ordovician (Katian)	E	4
A34	9.368(2)	6.893(4)	<i>Scabbardella altipes</i> (Henningsmoen, 1948)	Keisley, Westmorland (UK)	Late Ordovician (Katian)	E	4
A74	9.385(4)	6.876(5)	<i>Scabbardella altipes</i> (Henningsmoen, 1948)	Keisley, Westmorland (UK)	Late Ordovician (Katian)	E	4
A75	9.377(2)	6.878(4)	<i>Scabbardella altipes</i> (Henningsmoen, 1948)	Keisley, Westmorland (UK)	Late Ordovician (Katian)	E	4
A38	9.365(3)	6.885(2)	<i>Amorphognathus</i> sp. (Pa)	Cannamenda, Sardinia (Italy)	Late Ordovician (Katian)	E	5
A66	9.377(2)	6.876(3)	<i>Amorphognathus</i> sp. (Pa)	Cannamenda, Sardinia (Italy)	Late Ordovician (Katian)	E	5

A67	9.376(2)	6.888(3)	<i>Amorphognathus</i> sp. (Pa)	Cannamenda, Sardinia (Italy)	Late Ordovician (Katian)	E	5
A37	9.363(3)	6.887(4)	<i>Amorphognathus</i> sp. (Pb)	Cannamenda, Sardinia (Italy)	Late Ordovician (Katian)	E	5
A41	9.364(2)	6.905(3)	<i>Amorphognathus</i> sp. (Pb)	Cannamenda, Sardinia (Italy)	Late Ordovician (Katian)	E	5
A68	9.368(3)	6.883(4)	<i>Amorphognathus</i> sp. (Pb)	Cannamenda, Sardinia (Italy)	Late Ordovician (Katian)	E	5
A72	9.372(3)	6.887(6)	<i>Amorphognathus</i> sp. (Pb)	Cannamenda, Sardinia (Italy)	Late Ordovician (Katian)	E	5
A39	9.377(2)	6.871(6)	<i>Scabbardella altipes</i> (Henningsmoen, 1948)	Cannamenda, Sardinia (Italy)	Late Ordovician (Katian)	E	5
A40	9.376(2)	6.869(5)	<i>Scabbardella altipes</i> (Henningsmoen, 1948)	Cannamenda, Sardinia (Italy)	Late Ordovician (Katian)	E	5
A69	9.368(4)	6.885(8)	<i>Scabbardella altipes</i> (Henningsmoen, 1948)	Cannamenda, Sardinia (Italy)	Late Ordovician (Katian)	E	5
A70	9.373(2)	6.887(4)	<i>Scabbardella altipes</i> (Henningsmoen, 1948)	Cannamenda, Sardinia (Italy)	Late Ordovician (Katian)	E	5
A49	9.364(2)	6.884(3)	<i>Amorphognathus</i> sp. (Pa)	Saint-Hilaire-la-Gérard, Normandy (France)	Late Ordovician (Katian)	E	4-5
A50	9.367(3)	6.885(4)	<i>Amorphognathus</i> sp. (Pa)	Saint-Hilaire-la-Gérard, Normandy (France)	Late Ordovician (Katian)	E	4-5
A51	9.371(2)	6.884(2)	<i>Amorphognathus</i> sp. (Pa)	Saint-Hilaire-la-Gérard, Normandy (France)	Late Ordovician (Katian)	E	4-5
62	9.366(3)	6.887(3)	<i>Amorphognathus</i> sp. (Pb)	Saint-Hilaire-la-Gérard, Normandy (France)	Late Ordovician (Katian)	E	4-5
A52	9.371(2)	6.891(3)	<i>Amorphognathus</i> sp. (Pb)	Saint-Hilaire-la-Gérard, Normandy (France)	Late Ordovician (Katian)	E	4-5
A107	9.360(3)	6.887(3)	<i>Amorphognathus</i> sp. (Pb)	Saint-Hilaire-la-Gérard, Normandy (France)	Late Ordovician (Katian)	E	4-5
A108	9.364(3)	6.884(4)	<i>Amorphognathus</i> sp. (Pb)	Saint-Hilaire-la-Gérard, Normandy (France)	Late Ordovician (Katian)	E	4-5

17	9.357(4)	6.888(5)	<i>Amorphognathus</i> sp. (Sd)	Saint-Hilaire-la-Gérard, Normandy (France)	Late Ordovician (Katian)	E	4-5
68	9.379(2)	6.875(3)	<i>Hamarodus brevirameus</i> (Walliser, 1964) (M)	Saint-Hilaire-la-Gérard, Normandy (France)	Late Ordovician (Katian)	E	4-5
82	9.376(2)	6.880(3)	<i>Hamarodus brevirameus</i> (Walliser, 1964) (M)	Saint-Hilaire-la-Gérard, Normandy (France)	Late Ordovician (Katian)	E	4-5
49	9.365(2)	6.887(9)	<i>Hamarodus brevirameus</i> (Walliser, 1964) (Sc)	Saint-Hilaire-la-Gérard, Normandy (France)	Late Ordovician (Katian)	E	4-5
21	9.374(2)	6.880(2)	<i>Icriodella</i> sp.	Saint-Hilaire-la-Gérard, Normandy (France)	Late Ordovician (Katian)	E	4-5
20	9.374(4)	6.884(4)	<i>Panderodus</i> sp.	Saint-Hilaire-la-Gérard, Normandy (France)	Late Ordovician (Katian)	E	4-5
56	9.374(4)	6.867(6)	<i>Panderodus</i> sp.	Saint-Hilaire-la-Gérard, Normandy (France)	Late Ordovician (Katian)	E	4-5
A53	9.369(3)	6.878(6)	<i>Panderodus</i> sp.	Saint-Hilaire-la-Gérard, Normandy (France)	Late Ordovician (Katian)	E	4-5
24	9.369(2)	6.877(3)	<i>Sagittodontina robusta</i> Knüpfer, 1967 (Pa)	Saint-Hilaire-la-Gérard, Normandy (France)	Late Ordovician (Katian)	E	4-5
41	9.372(2)	6.886(5)	<i>Sagittodontina robusta</i> Knüpfer, 1967 (Pa)	Saint-Hilaire-la-Gérard, Normandy (France)	Late Ordovician (Katian)	E	4-5
46	9.368(6)	6.876(5)	<i>Sagittodontina robusta</i> Knüpfer, 1967 (Sd)	Saint-Hilaire-la-Gérard, Normandy (France)	Late Ordovician (Katian)	E	4-5
45	9.375(3)	6.884(5)	<i>Scabbardella altipes</i> (Henningsmoen, 1948)	Saint-Hilaire-la-Gérard, Normandy (France)	Late Ordovician (Katian)	E	4-5
59	9.375(4)	6.880(3)	<i>Scabbardella altipes</i> (Henningsmoen, 1948)	Saint-Hilaire-la-Gérard, Normandy (France)	Late Ordovician (Katian)	E	4-5
60	9.381(2)	6.881(2)	<i>Scabbardella altipes</i> (Henningsmoen, 1948)	Saint-Hilaire-la-Gérard, Normandy (France)	Late Ordovician (Katian)	E	4-5
91	9.368(2)	6.877(4)	<i>Scabbardella altipes</i> (Henningsmoen, 1948)	Saint-Hilaire-la-Gérard, Normandy (France)	Late Ordovician (Katian)	E	4-5
103	9.374(3)	6.908(4)	<i>Scabbardella altipes</i> (Henningsmoen, 1948)	Saint-Hilaire-la-Gérard, Normandy (France)	Late Ordovician (Katian)	E	4-5

A54	9.361(2)	6.906(5)	<i>Scabbardella altipes</i> (Henningsmoen, 1948)	Saint-Hilaire-la-Gérard, Normandy (France)	Late Ordovician (Katian)	E	4-5
A22	9.379(2)	6.889(2)	<i>Rhipidognathus symmetricus</i> Branson, Mehl and Branson, 1951	Saluda Dolomite (USA)	Late Ordovician	E	1
A23	9.363(3)	6.897(4)	<i>Panderodus</i> sp.	Saluda Dolomite (USA)	Late Ordovician	E	1
A104	9.374(3)	6.887(4)	<i>Belodina</i> sp.	Kimmswick Formation, Missouri (USA)	Late Ordovician	E	1
A105	9.359(3)	6.878(4)	<i>Plectodina</i> sp.	Kimmswick Formation, Missouri (USA)	Late Ordovician	E	1
A106	9.379(2)	6.886(4)	<i>Panderodus</i> sp.	Kimmswick Formation, Missouri (USA)	Late Ordovician	E	1
A1	9.368(4)	6.857(6)	<i>Zieglerodina planilingua</i> (Murphy & Valenzuela-Ríos, 1999)	U Topolů (Bohemia)	Early Devonian (Lochkovian)	E	3
A2	9.383(3)	6.885(3)	<i>Lanea omoalpha</i> (Murphy & Valenzuela-Ríos, 1999)	U Topolů (Bohemia)	Early Devonian (Lochkovian)	E	3
A82	9.370(3)	6.894(3)	<i>Palmatolepis</i> sp.	Pramosio A, Carnic Alps (Italy)	Late Devonian (Frasnian)	E	4.5
A83	9.376(2)	6.883(6)	<i>Polygnathus decorosus</i> Stauffer, 1938	Pramosio A, Carnic Alps (Italy)	Late Devonian (Frasnian)	E	4.5
A80	9.362(3)	6.886(4)	unrecognizable fragment	Casera Collinetta di Sotto A, Carnic Alps (Italy)	Late Devonian (Famennian)	E	4.5
A81	9.371(3)	6.881(6)	<i>Branmehla weneri</i> (Ziegler, 1957)	Casera Collinetta di Sotto A, Carnic Alps (Italy)	Late Devonian (Famennian)	E	4.5
A101	9.365(2)	6.878(3)	<i>Palmatolepis triangularis</i> Sannemann, 1955	Texas (USA)	Late Devonian (Famennian)	E	2
A102	9.384(1)	6.886(2)	<i>Palmatolepis subperlobata</i> Branson and Mehl, 1934	Texas (USA)	Late Devonian (Famennian)	E	2
A103	9.378(2)	6.879(3)	<i>Icriodus</i> sp.	Texas (USA)	Late Devonian (Famennian)	E	2
A76	9.377(2)	6.871(3)	unrecognizable fragment	Dolina, Carnic Alps (Italy)	Carboniferous Early Mississippian (Tournaisian)	E	4.5

A77	9.356(2)	6.882(2)	unrecognizable fragment	Dolina, Carnic Alps (Italy)	Carboniferous Early Mississippian (Tournaisian)	E	4.5
A100	9.370(2)	6.882(3)	unrecognizable fragment	Dolina, Carnic Alps (Italy)	Carboniferous Early Mississippian (Tournaisian)	E	4.5
A78	9.374(2)	6.884(3)	<i>Gnathodus</i> sp.	Dolina, Carnic Alps (Italy)	Carboniferous Middle Mississippian (Visean)	E	4-4.5
A79	9.370(2)	6.887(4)	<i>Gnathodus</i> sp.	Dolina, Carnic Alps (Italy)	Carboniferous Middle Mississippian (Visean)	E	4-4.5
A86	9.374(2)	6.878(3)	<i>Pachycladina obliqua</i> Staesche, 1964	Cencenighe Galleria, Dolomites (Italy)	Early Triassic (Olenekian)	E	5.5-6
A87	9.363(2)	6.904(5)	<i>Pachycladina obliqua</i> Staesche, 1964	Cencenighe Galleria, Dolomites (Italy)	Early Triassic (Olenekian)	E	5.5-6
A84	9.355(3)	6.888(3)	unrecognizable fragment	Sotto le Rive, Dolomites (Italy)	Middle Triassic (Anisian)	E	1.5
A85	9.362(4)	6.881(5)	unrecognizable fragment	Sotto le Rive, Dolomites (Italy)	Middle Triassic (Anisian)	E	1.5
A42	9.372(2)	6.884(2)	<i>Carnepigondolella pseudodiebeli</i> (Kozur, 1972)	Pizzo Mondello, Sicani Mountains, Sicily (Italy)	Late Triassic (Carnian)	E	1.5
A43	9.383(3)	6.883(4)	<i>Carnepigondolella pseudodiebeli</i> (Kozur, 1972)	Pizzo Mondello, Sicani Mountains, Sicily (Italy)	Late Triassic (Carnian)	E	1.5
A44	9.382(2)	6.881(3)	<i>Carnepigondolella pseudodiebeli</i> (Kozur, 1972)	Pizzo Mondello, Sicani Mountains, Sicily (Italy)	Late Triassic (Carnian)	E	1.5

Table SI-1b. Bioapatite cell parameters calculated for other phosphatic/phosphatized fauna.

Code	<i>a</i> (Å)	<i>c</i> (Å)	Taxa	Locality/Formation	Age
A16	9.356(4)	6.900(4)	ostracod	Kinneulle, Västergötland (Sweden)	Cambrian Furongian (Paibian)
A17	9.353(4)	6.903(3)	ostracod	Kinneulle, Västergötland (Sweden)	Cambrian Furongian (Paibian)
A92	9.349(4)	6.900(3)	ostracod	Kinneulle, Västergötland (Sweden)	Cambrian Furongian (Paibian)
A93	9.346(6)	6.908(6)	ostracod	Kinneulle, Västergötland (Sweden)	Cambrian Furongian (Paibian)
A94	9.338(7)	6.885(7)	ostracod	Kinneulle, Västergötland (Sweden)	Cambrian Furongian (Paibian)
A95	9.358(5)	6.905(4)	undetermined	Kinneulle, Västergötland (Sweden)	Cambrian Furongian (Paibian)
A96	9.345(2)	6.909(3)	undetermined	Kinneulle, Västergötland (Sweden)	Cambrian Furongian (Paibian)
A97	9.356(6)	6.899(4)	undetermined	Kinneulle, Västergötland (Sweden)	Cambrian Furongian (Paibian)
A7	9.354(1)	6.887(2)	brachiopod	Öland (Sweden)	Early Ordovician (Tremadocian)
A8	9.335(5)	6.887(5)	brachiopod	Öland (Sweden)	Early Ordovician (Tremadocian)
A25	9.367(2)	6.892(2)	brachiopod	Keisley, Westmorland (UK)	Late Ordovician (Katian)
A26	9.368(3)	6.892(3)	brachiopod	Keisley, Westmorland (UK)	Late Ordovician (Katian)
A73	9.366(2)	6.880(2)	brachiopod	Cannamenda, Sardinia (Italy)	Late Ordovician (Katian)
A36	9.362(2)	6.888(2)	brachiopod	Cannamenda, Sardinia (Italy)	Late Ordovician (Katian)
A55	9.337(3)	9.868(3)	brachiopod	Saint-Hilaire-la-Gérard, Normandy (France)	Late Ordovician (Katian)
A64	9.372(2)	6.890(2)	brachiopod	Saint-Hilaire-la-Gérard, Normandy (France)	Late Ordovician (Katian)
A3	9.343(3)	6.897(3)	brachiopod	U Topolů (Bohemia)	Early Devonian (Lochkovian)
A4	9.345(3)	6.891(3)	brachiopod	U Topolů (Bohemia)	Early Devonian (Lochkovian)
A35	9.365(1)	6.896(2)	bryozoan	Cannamenda, Sardinia (Italy)	Late Ordovician (Katian)
A71	9.351(2)	6.884(4)	bryozoan	Cannamenda, Sardinia (Italy)	Late Ordovician (Katian)
A58	9.368(3)	6.889(3)	bryozoan	Saint-Hilaire-la-Gérard, Normandy (France)	Late Ordovician (Katian)

A61	9.371(2)	6.891(2)	bryozoan	Saint-Hilaire-la-Gérard, Normandy (France)	Late Ordovician (Katian)
A65	9.372(3)	6.887(4)	bryozoan	Saint-Hilaire-la-Gérard, Normandy (France)	Late Ordovician (Katian)
A24	9.361(2)	6.893(3)	bryozoan	Saluda Dolomite (USA)	Late Ordovician
A45	9.337(3)	6.901(3)	fish tooth	Pizzo Mondello, Sicani Mountains, Sicily (Italy)	Late Triassic (Carnian)
A46	9.343(5)	6.896(4)	fish tooth	Pizzo Mondello, Sicani Mountains, Sicily (Italy)	Late Triassic (Carnian)
A47	9.411(6)	6.881(5)	fish tooth	Pizzo Mondello, Sicani Mountains, Sicily (Italy)	Late Triassic (Norian)