Exceptional preservation requires fast biodegradation: the case study of thylacocephalan specimens from La Voulte-sur-Rhône (Callovian, Jurassic, France)

Clément Jauvion, Sylvain Bernard, Pierre Gueriau, Cristian Mocuta, Sylvain Pont, Karim Benzerara, Sylvain Charbonnier

► To cite this version:

Clément Jauvion, Sylvain Bernard, Pierre Gueriau, Cristian Mocuta, Sylvain Pont, et al.. Exceptional preservation requires fast biodegradation: the case study of thylacocephalan specimens from La Voulte-sur-Rhône (Callovian, Jurassic, France). *Palaeontology*, 2020, 63 (3), pp.395-413. 10.1111/pala.12456 . hal-03022427

HAL Id: hal-03022427

<https://hal.science/hal-03022427>

Submitted on 24 Nov 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

**Exceptional preservation requires fast biodegradation:
the case study of thylacocephalan specimens from La Voulte-sur-Rhône
(Callovian, Jurassic, France)**

Clément Jauvion^{1,2,*}, Sylvain Bernard¹, Pierre Gueriau^{3,4,5},

Cristian Mocuta⁴, Sylvain Pont¹, Karim Benzerara¹ and Sylvain Charbonnier²

¹*Muséum national d'Histoire naturelle, Sorbonne Université, CNRS UMR 7590, IRD, Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie, IMPMC, Paris (France); email:clement.jauvion@mnhn.fr*

²*Muséum national d'Histoire naturelle, Sorbonne Université, CNRS UMR 7207, CR2P, Centre de Recherche en Paléontologie - Paris, 8 rue Buffon, 75005 Paris (France); email:clement.jauvion@mnhn.fr*

³*IPANEMA, CNRS, ministère de la Culture, UVSQ, USR3461, Université Paris-Saclay, F-91192 Gif-sur-Yvette (France)*

⁴*Synchrotron SOLEIL, BP 48 Saint-Aubin, F-91192 Gif-surYvette (France)*⁵*Current address: Institute of Earth Sciences, University of Lausanne, Géopolis, CH-1015 Lausanne, Switzerland*

**Corresponding Author*

Abstract

Konservat-Lagerstätten are seen as snapshots of past biodiversity for a given location and time. Yet, processes leading to the exceptional morphological preservation of fossils in these deposits remain incompletely understood. This results in the deficient assessment of taphonomic biases and limits the robustness/relevance of palaeobiological reconstructions. Here, we report the mineralogical characterization of crustacean fossils preserved within carbonate-rich concretions from the Jurassic Konservat-Lagerstätte of La Voulte-sur-Rhône (Ardèche, France). The combination of SEM-EDS, TEM, synchrotron-based XRF, XRD and XANES allows identifying the mineralogical phases composing these fossils (i.e. fluorapatite, Fe-sulfides (pyrite, pyrrhotite) and Mg-calcite) and the surrounding matrix (i.e. Mg-calcite, clays and detrital silicates). Fluorapatite and pyrite (and pyrrhotite) precipitated during decay under anoxic conditions, replacing delicate organic structures and preserving anatomical details. These mineral structures were subsequently consolidated by a Mg-calcite cement. Of note, histologically similar tissues were replaced by the same mineral phases, confirming that ‘fossilization [in La Voulte] occurred rapidly enough to be influenced by tissue composition’. Altogether, the present study shows that exceptional preservation requires fast biodegradation, thereby confirming recent experimental evidence.

Key words: Konservat-Lagerstätten; fossilization; exceptional preservation; mineralogy, arthropod.

The fossil record is far from delivering an accurate picture of past biodiversity (e.g. Kidwell and Flessa 1995). In some rare instances, the soft tissues of animals and plants can be replaced by mineral phases that preserve anatomical details at a very fine scale (Seilacher 1970). Still, biological, anatomical and environmental reconstructions may suffer from biases directly related to the taphonomic history of investigated fossils. Thus, improving the robustness of paleontological reconstructions requires identifying and quantifying potential taphonomic biases.

Although they provide invaluable assets to understand the otherwise complex natural systems (Briggs and McMahon 2016; Wilson *et al.* 2016; Purnell *et al.* 2018), decay experiments must be viewed with caution since they do not entirely mimic early fossilization processes (Parry *et al.* 2018). Therefore, and because of the complexity of natural systems (e.g. Briggs and McMahon 2016; Wilson *et al.* 2016), documenting the geochemistry and mineralogy of natural fossil appears necessary to genuinely constrain advanced fossilization processes (Wilby 2001; Xiao and Schiffbauer 2009; Bernard *et al.* 2010; Galvez *et al.* 2012; Cosmidis *et al.* 2013a, b; Schiffbauer *et al.* 2014; Robin *et al.* 2015, 2018; Sansom *et al.*, 2016).

The 165 Ma Konservat-Lagerstätte of La Voulte-sur-Rhône (Ardèche, France, Fig. 1A) is renowned worldwide for the high degree of morphological preservation of its fossils and for the diversity of its content in invertebrate fauna, especially arthropods (Secretan 1985; Fischer 2003; Charbonnier *et al.* 2007a, 2010; Charbonnier 2009; Audo *et al.* 2014b, a, 2016, 2019, Jauvion *et al.* 2017, 2016; Audo and Schweigert 2018) and cephalopods (Fischer and Riou 1982, 2002; Fischer 2003; Kruta *et al.* 2016).

Despite exceptional preservation, many details of the anatomy of these fossils have been lost. For instance, the fossils investigated here do not display any remains of their nervous system nor their gonadal tissues. Based on thorough investigations, Wilby *et al.* (1996) proposed a taphonomic scenario for the La Voulte fossils, including a diagenetic sequence of mineral precipitation: apatite → calcite ± gypsum → pyrite ± chalcopyrite → galena.

Here, following (Wilby *et al.* 1996) and using the methodology adopted by early geobiology studies (Benzerara *et al.* 2005, 2006; Bernard *et al.* 2007; Lepot *et al.* 2008), we investigate the geochemical and mineralogical nature of specimens of thylacocephalan arthropod *Dollocaris ingens* Van Straelen 1923 preserved in three dimensions within nodules from the La Voulte Konservat-

Lagerstätte (Fig. 1B–C). The comparison between specimens allows revisiting the diagenetic sequence of mineral precipitation proposed by Wilby *et al.* (1996), while geochemical calculations allows critically testing its thermodynamic feasibility, thereby shedding new light on the processes having led to exceptional preservation in the La Voulte-sur-Rhône Konservat-Lagerstätte.

MATERIAL AND METHODS

Material

The investigated fossils are specimens of thylacocephalan *Dollocaris ingens* Van Straelen, 1923 preserved in 3D within nodules from the 165 Ma La Voulte Konservat-Lagerstätte. The La Voulte fossiliferous site lays on the western margin of the Tethys Ocean, adjacent to the Hercynian Massif Central, which was probably submerged (Charbonnier *et al.* 2007b). A complex palaeotopography of tilted blocks indicates a depth of probably more than 200 m (Charbonnier *et al.* 2007b, 2014). The La Voulte Lagerstätte is found in the Ravin des Mines locality. The lithology of the fossiliferous site is composed of marls (5-6 m) topped by 15 m of iron carbonate deposits, which were exploited in the 19th century. The fossiliferous nodules, as described here, are very abundant in the basal marls. Terrigenous sediments at least partly originate from the submerged orogen, whereas carbonate were produced in platforms developed on the same Massif (Elmi 1990a, b). Of note, hydrothermalism probably took place in the La Voulte palaeoenvironment.

The specimens investigated here (Fig. 2) are part of the Muséum national d'Histoire naturelle (MNHN; French National Museum of Natural History, Paris) collections. Thylacocephalans are extinct arthropods known from the Early Silurian (or, possibly, Cambrian) to the Late Cretaceous, with possible crustacean affinity (Pinna *et al.* 1982; Secretan 1983, 1985; Secretan and Riou 1983; Schram *et al.* 1999; Lange *et al.* 2001; Vannier *et al.* 2006; Haug *et al.* 2014; Schram 2014; Broda *et al.* 2015; Charbonnier *et al.* 2017). Following Wilby *et al.* (1996), we prepared petrographic thin sections (specimens

MNHN.F.A70114 and MNHN.F.A70115) for optical microscopy and polished sections (specimens MNHN.F.R06054 and MNHN.F.A66910 for SEM and synchrotron-based XRF and XRD. Ca-XANES and TEM data were collected on FIB foils extracted from these polished sections.

Methods

Powder XRD. The ‘bulk’ mineralogical composition of the different organs of the fossils and the mineral matrix was assessed using a conventional Cu-K α ($\lambda = 1.5418 \text{ \AA}$) powder diffractometer (D2 Phaser, Bruker, Germany) at the SOLEIL Synchrotron chemistry laboratory. About 5-10 mm³ of each organ (heart, gills, appendage) and of the matrix were sawed out from a thick section of MNHN.F.A66910. The different parts were separately and finely crushed into powder using an agate mortar. The system is equipped with a Ceramic KFL X-ray tube source and a 1D-linear LynxEye detector. The following experimental conditions were used: 30 kV acceleration voltage; 10 mA filament current; 10–70 degrees 2θ range; 0.02 degree angular step, 0.5 s and 1 s counting time for the fossil tissues and matrix, respectively. Phase identification was carried out using the EVA software (Bruker), using the ICDD PDF-4 Minerals database.

Optical microscopy. Petrographic thin sections were observed using a Leica DMXRA microscope (IMPMC, Paris, France), equipped with a Märzhäuser Wetzlar motorized stage. Images were captured with an Olympus DP72 camera, controlled with the Cell (Olympus, v. 3.4) software.

FIB, SEM & TEM. Fossil specimens were characterized using a Zeiss Ultra 55 FEG-SEM operating at IMPMC (Paris, France) and equipped with a Bruker EDS QUANTAX detector (Bruker Corporation, Houston, TX, USA). Focused ion beam (FIB) milling was performed at low Ga-ion currents using the FEI STRATA DB 235 FIB system operating at the IEMN (Lille, France) to prepare electron and soft X-ray transparent $\sim 15 \mu\text{m} \times 5 \mu\text{m} \times 80 \text{ nm}$ cross-sections. TEM observations of FIB sections were carried out on the 200 kV JEOL 2100 FEG-TEM (JEOL Ltd, Tokyo, Japan) operating at IMPMC (Paris,

France). Elemental mapping by EDS and scanning transmission electron microscopy (STEM) imaging were conducted in high-angle annular dark field (HAADF) mode.

Synchrotron-based XRF & XRD. Major-to-trace elemental and mineralogical compositions were determined on the DiffAbs beamline at SOLEIL Synchrotron (Baudalet *et al.* 2005). The incident X-ray beam (of 18–18.2 keV energy) was monochromatized (10^{-4} resolution) using a Si(111) double-crystal monochromator and focused / collimated down to 10 or several tens of microns using either Kirkpatrick-Baez mirrors (Kirkpatrick and Baez 1948) or pin holes respectively. A micrometer precision XYZ scatter stage is used to laterally scan the sample in the X-ray beam. X-ray fluorescence was collected in reflection geometry using a 4-element silicon drift detector (SDD, Vortex ME4, total active area: 170 mm²) placed at 90 degrees to the incident beam, in the horizontal plane. X-ray diffraction was recorded in transmission geometry using a 2D pixel area detector (XPAD s140; Delpierre *et al.* 2007; Medjoubi *et al.* 2010; Le Bourlot *et al.* 2012). The area detector covers a wide 2θ range (more than 10 degrees) in a single image, range which can be extended as well by moving its position. The recorded images are converted into Intensity vs 2θ diffractograms using an in-house developed code (Mocuta *et al.* 2013; Cook *et al.* 2018). Combined with the use of high energy (18 keV) X-rays, a diffractogram extracted from a single detector image is enough to exhibit all main peaks necessary to identify, in combination with the results from the other techniques, the present crystalline phases. Phase identification was carried out using the EVA software (Bruker) and the ICDD PDF-4 Minerals database. Simultaneous XRF and XRD mapping of entire fossils at a 15–75 μm lateral resolution was performed using the multi-technique FLYSCAN scanning developed at SOLEIL (Leclercq *et al.* 2015). At each pixel, both a full XRF spectrum and an XRD signal (the XPAD detector fixed at a given 2θ position) were collected with a 10–60 ms dwell time. All elemental and mineralogical distributions presented herein correspond to intensities in XRF and XRD (reconstructed diagrams) peaks.

Synchrotron-based XANES spectroscopy. XANES data were collected at the Ca L-edge on the STXM Polymer beamline (5.3.2.2) at the ALS (Kilcoyne *et al.* 2003) and the HERMES STXM beamline at SOLEIL Synchrotron (Belkhou *et al.* 2015; Swaraj *et al.* 2017). The microscope chambers were

pumped down to less than 100 mTorr after sample insertion. Energy calibration was done using the well-resolved 3p Rydberg peak of gaseous CO₂ at 294.96 eV. On the upstream side of the microscope chamber, the optical elements of the HERMES beamline are exposed to a continuous flow of pure O₂ to remove carbon contamination (Swaraj *et al.* 2017). X-ray absorption spectroscopy was performed by collecting image stacks with a spatial resolution of 25 nm, that is, by rastering selected areas of samples in the x–y directions at energy increments of 0.1 eV over the calcium energy range (245–255 eV). Stack measurements were performed with a dwell time ≤ 1 ms per pixel to prevent irradiation damage. Alignment of images of stacks and extraction of XANES spectra were done using the aXis2000 software (ver2.1n). Spectral peak positions were determined using the Athena software package (Ravel and Newville 2005). The XANES spectra shown in the present contribution correspond to homogeneous areas of several hundreds of square nanometres.

Geochemical calculations. The software PHREEQC3 (Parkhurst and Appelo 2013) was used with the Thermoddem database (Blanc *et al.* 2012) to ensure the thermodynamic feasibility of the proposed sequence of mineral precipitation at various temperatures (from 20 to 200°C, at 20 bar) and pressures (from 1 to 30 bar, at 80°C). A modified seawater composition (Appelo and Postma 2005) was used to simulate a hydrothermal environment with decaying carcasses under anoxic conditions (see Table 1). Also, this solution was set in equilibrium with Mg-illite and kaolinite to reflect sediment mineralogical composition. Note that a quite simplistic advective-diffusive transport model (10 cells, 250 pore volume injection cycles of 1 hour; diffusion coefficient: $2.5 \cdot 10^{-9}$ m²/s; at 20 bar and 80°C) was used to model the later phase transformation (oxidation). The injected fluid chemistry is summarized in Table 1.

RESULTS

Organ morphologies

The fossil specimens of *D. ingens* investigated here display exceptionally preserved anatomical details (Charbonnier 2009; Vannier *et al.* 2016). The heart structure is similar to that of modern crustaceans (Mayrat 1994, Figs 2B, D, 3A) and many muscular fibres and hemolymphatic vessels can be observed (Figs. 2B–D, 3B, 4A, D). The stomach ends on a valve (Figs 2C, 4B, E), i.e. a papillae-bearing structure that separates it from the intestines. Moreover, shell fragments, probably belonging to other smaller crustaceans, can be observed within the stomach of some specimens. The hepatopancreas structure is similar to that of modern crustaceans (Icely and Nott 1992; Ceccaldi 1994; Esteve and Herrera 2000) and exhibits its acini (or caeca – Figs. 2C, 4B, E). Note that neither the nervous system nor gonadal tissues can be observed.

Chemical element distribution

The fossil specimens of *D. ingens* investigated here are chemically heterogeneous (Fig. 2D). Synchrotron-based XRF maps show that muscles, the heart and the hemolymphatic vessels are rich in Y and Pb, whereas the cuticle is enriched in Y (Fig. 5). The gills and the hepatopancreas display quite high Pb concentrations but no Y (Fig. 5B, D). Areas rich in Sr, such as the valve for instance, do not contain Pb (Fig. 5C–D). Zn-rich areas appear throughout the fossils, mainly, near areas enriched in Pb (Fig. 5B, D).

Of note, the distribution of Y can be seen as that of apatite, while the distribution of Sr in areas impoverished in Y can be seen as that of calcite (Gueriau *et al.* 2018). The distributions of Zn and Pb likely correspond to that of sulfides, namely wurtzite (ZnS) and galena (PbS) (e.g., Wilby *et al.*, 1996). The distribution of Rb corresponds to that of (likely detrital) silicate minerals.

SEM-EDX observations reveal that the heart is composed of P-rich fibres surrounded by a Fe- and S-rich layer (Fig. 4A). Some Si-rich minerals are also present near the fibres. The hepatopancreas is composed of Fe and S, while the valve mainly contains Ca (Fig. 4B, E, G). Si-rich phases are overlying hepatopancreatic structures (Fig. 4B, E, G). Some areas exhibit framboid-like minerals rich in Fe and O (Fig. 4C, F) associated with minerals rich in S and Mg. Besides clearly recognizable structures, the main volume (‘background signal’) of the fossil is P-poor and Ca-rich, and shows traces of Mg (Fig. 4).

Mineral phases

Powder XRD indicates that the main mineral phases composing the investigated fossils are Mg-calcite ((Ca,Mg)CO₃), fluorapatite (Ca₅(PO₄)₃(OH,F)), wurtzite (ZnS), pyrite (FeS₂), pyrrhotite (Fe₇S₈) and opal-CT (SiO₂(H₂O)_n) (Fig. 6A). Additional mineral phases are argentopyrite (AgFe₂S₃), arsenopyrite (FeAsS), pentlandite ((Fe,Ni)₉S₈), dolomite (CaMg(CO₃)₂), epsomite (MgSO₄·7H₂O), halloysite-7 Å (Al₂(Si₂O₅)(OH)₄), illite ((K,H₃O)(Al,Mg,Fe)₂(Si,Al)₄O₁₀[(OH)₂,(H₂O)]) and shortite (Na₂Ca₂(CO₃)₃). Note that argentopyrite is only found in the gills and the appendage, and dolomite is only found in the heart.

Petrographic observations (Fig. 3) on thin sections reveal that the lumen of the heart is composed of calcite, surrounded by fluorapatite (Fig. 3A). The muscular fibres (Fig. 3B) are composed of fluorapatite, with sulfides (pyrrhotite and associated forms) outlining bundles of fibres and calcite filling the rest of the area. Some structures show prismatic fluorapatite crystals growing along a preferential petrographic direction, directly on organic layers, with prismatic crystals of calcite in the continuity (Figs. 3C). The gills display a microcrystalline structure with fluorapatite/pyrite associations (Fig. 3A).

XRD maps confirm the fluorapatite nature of the cuticle and muscle fibres (Fig. 6B, D). Mg-calcite can be observed in the heart and the valve (Figs. 5A, 6D), as well as in areas where no organ was morphologically preserved. Pyrite and pyrrhotite are located in the muscles. Pyrite is also located in the gills, close to the cuticle and the matrix (Figs. 6B–C). Arsenopyrite seems to be restricted to muscle fibres, including the appendages, while wurtzite is mainly located at the periphery of the fossils. Other sulfides, such as galena, are also identified, but not detected with XRD (Fig. 5 and SEM-EDX observations). Opal-CT is observed in the vicinity of Fe-sulfides (Fig. 6D).

STXM-based XANES investigations at the Ca L-edge confirm the presence of apatite within muscle fibres and the presence of Mg-rich carbonates (see Cosmidis and Benzerara 2014 and Zougrou *et al.* 2016 for comparison) (Fig. 7A). STEM observations (Fig. 7B–C) confirm that pyrite and

fluorapatite are automorphous, in contrast to Mg-calcite that has grown in between pyrite and fluorapatite crystals.

Summary

Chemical and mineralogical compositions of the different organs of the investigated fossils are summarized in Table 2. It emerges that histologically comparable tissues now display similar mineralogical composition. Muscles fibres are mainly composed of fluorapatite outlined by pyrite, arsenopyrite and pyrrhotite with voids filled by calcite and in some parts, opal-CT. The heart and the hemolymphatic vessels are composed of apatite and Fe-sulfides, probably pyrite, pyrrhotite and arsenopyrite. The lumina of the heart displays a mineralogical infill in Mg-rich calcite and dolomite. The hepatopancreas is composed of pyrite while the valve is composed of Mg-rich calcite. The gills are made of pyrite and argentopyrite. The cuticle is composed of fluorapatite. The sedimentary matrix at the proximity of the fossil is rich in Mg-calcite associated with pyrite and wurtzite, epsomite and silicate minerals (incl. clays).

DISCUSSION

Time sequence of mineral precipitation

The fossil specimens of *D. ingens* investigated here are mineralogically heterogeneous. Following Wilby *et al.* (1996), we propose here a tentative precipitation time sequence of the mineral phases composing the fossils based on their textural and structural relationships. A summary of the proposed sequence is displayed as a flow chart in Fig. 10.

The observations reported here suggest that fluorapatite and sulfide minerals (pyrite, arsenopyrite, argentopyrite, pyrrhotite and pentlandite) minerals precipitated concomitantly (as did

galena and wurtzite), before Mg-calcite and opal-CT that precipitated secondarily, thus filling up the space left between preserved structures. This contrasts with the conclusions of Wilby *et al.* (1996), where apatite only was first to precipitate. Of note, the prismatic morphology observed for fluorapatite can also be interpreted as a sign of encrustation on a probable organic structure, thus replicating the morphology (Xiao and Schiffbauer 2009; Schiffbauer *et al.* 2014).

The presence of Mg-sulfates such as epsomite and of Fe-oxides displaying framboid-like structures within the fossils (Figs. 4C, F, 5 and 6B–D) likely results from an intrusion of not yet indurated clay-rich sedimentary material having oxidized pyrite framboids. Of note, these oxidized framboidal structures retained a high concentration of S in the innermost parts of the particles, confirming their original sulfidic nature. This intrusion thus occurred after the precipitation of fluorapatite and pyrite. Such an event was not reported or discussed by Wilby *et al.* (1996).

Thermochemical calculations confirm that the co-precipitation of fluorapatite, sulfide minerals (mainly pyrite), galena and sphalerite (instead of wurtzite) is possible in a hydrothermal environment similar to that of La Voulte, whatever the temperature and water depth (no influence of pressure in the 1-30 bar range was found; Fig. 8). The model also indicates that calcite and dolomite could have precipitated concomitantly (Fig. 8), which was likely the case within the nodules.

We used an advective-diffusive transport model to investigate the later oxidation event caused by the intrusion of not yet indurated clay-rich sedimentary material. A theoretical oxidative solution (rich in O₂ and SO₄²⁻, cf Table 1) was injected in the system. This model (Fig. 9) confirms that the oxidation of sulfides into sulfates and Fe-oxides can be related to a simple Redox condition change linked with local ‘fluid’ circulation within the carcass/fossil.

According to these simulations, anhydrite precipitates, even though only epsomite was observed within the fossils investigated. This may be due to the present simulations not taking into account kinetic effects nor the potential role played by bacteria. The same is true for wurtzite vs sphalerite, sulfate-reducing bacteria possibly inducing the precipitation of both (Moreau *et al.* 2004).

Conditions and processes having led to exceptional preservation

The exceptional preservation of the La Voulte fossils appears to result from the early replacement of soft tissues by mineral phases. Here, the earliest phases, which are also underlying and replicating the preserved anatomical structures are fluorapatite and pyrite. This is totally consistent with experimental studies that depicted the fast (in a matter of weeks) replacement of soft tissues by Ca-phosphates, including the muscles, the hepatopancreas and, sometimes, the cuticles of different crustaceans such as decapods and stomatopods (Briggs *et al.* 1993; Briggs and Kear 1994; Hof and Briggs 1997; Sagemann *et al.* 1999).

The precipitation of Ca-carbonates or Ca-phosphates has been compared to a ‘switch’, controlled by the decay-induced pH (low for phosphates, high for carbonates) and the effect of this precipitation on the relative concentrations of dissolved species (Allison 1988; Briggs and Kear 1994; Briggs and Wilby 1996). In open systems, the products of organic matter degradation (e.g. HCO_3^- and HS^-) may diffuse away, leading to the formation of a basic environment favouring carbonate precipitation. In contrast, in closed systems, the increasing organic matter degradation will decrease the pH, thereby favouring phosphate precipitation.

Here, the early precipitation of fluorapatite and pyrite points to an initially closed/acidic system. Note that the system could have been closed only apparently, with only local enrichments in acidic ions due to low diffusion rates, as suggested by concretion formation models (Raiswell 1993; Raiswell *et al.* 1993). Such conditions may have been created because of the presence of a microbial mat that acted as a sarcophagus (Iniesto *et al.* 2013, 2015, 2016, Raff *et al.* 2013, 2014).

The precipitation of Mg-rich calcite likely occurred because of local pH variations, potentially due to an opening of the system. This precipitation, also leading to nodule formation, also acted a protective layer regarding finely, morphologically replicated, organic structures, thus safeguarding preservation quality. Local pH variations have been previously invoked to explain the co-occurrence of Ca-phosphates and Ca-carbonates in a single fossil (Briggs and Kear 1993, 1994; Hof and Briggs 1997; Sagemann *et al.* 1999). As did the Mg-calcite within the fossils investigated here, calcite precipitated in these experiments as bundles or sheets with no apparent connection with decaying tissues. Similarly, the precipitation of Fe-oxides and epsomite likely resulted from the oxidation of pyrite (and other Fe-sulfides) and fluorapatite because of the intrusion within decaying carcasses of not yet indurated

sedimentary material, and therefore relatively early in the diagenetic sequence. Sediment movement in Konservat-Lagerstätten has already been suspected in the Burgess Shale, there, by bioturbation (Pratt and Kimmig 2019). The authors imply that the depositional environment might have been at least sometimes oxic. The association of sedimentary movement and temporary oxic conditions could match what we observe in La Voulte fossils, pushing toward a dynamic interpretation of environmental parameters favouring exceptional preservation.

Influence of the initial nature of the different tissues

The specimens investigated here are mineralogically heterogeneous, but tissues originally chemically similar now display similar mineralogical composition (Table 2). In fact, the cuticle and muscle fibres are mainly replaced by phosphates, while the valve and the lumen of the heart and hemolymphatic vessels are replaced/filled by/with Mg-rich carbonates and the hepatopancreas and the gills by sulfides. However, no evident correlation seems to exist between the nature of the mineral phases and the putative original cationic chemical composition of the different tissues (Table 3) (Pourang and Amini 2001; Baboli *et al.* 2013; Io and Ha 2013).

Although gonadal and neuronal tissues (such as optical nerves) were described in another crustacean from La Voulte (a polychelidan lobster; Jauvion *et al.* 2016), no remains of such tissues can be observed in the specimens investigated here. Rather than concluding on the absence of such tissues in thylacocephalans, it may be assumed that neuronal and gonadal tissues of polychelidans and thylacocephalans were not similarly resistant to decay, i.e. that they were chemically different. In fact, differential rate of decay and associated character loss has been proposed to explain preservation discrepancies (within a single organism) and taphonomic bias within Konservat-Lagerstätten (Sansom *et al.* 2010, 2011, 2013; Casenove *et al.* 2011; Murdock *et al.* 2014; Sansom 2016).

Although guts and gills are generally less decay-resistant than muscle fibres and cuticles, all these organs were replaced here by similar phases, i.e. Fe-sulfides more or less associated with Ca-phosphates. The observations reported here thus suggest that the precipitation of mineral phases was

342 primarily controlled by the variation of the chemical composition of the fluid over time (through local
343 ion availability and system ‘openness’) and/or by the different metabolisms of the microorganisms
344 involved in decay, rather than by the intrinsic resistance to decay of these organs. Altogether, the present
345 study confirms one of the the conclusions drawn by Wilby *et al.* (1996), i.e. that in La Voulte,
346 ‘fossilization occurred rapidly enough to be influenced by tissue composition’.

347 It clearly appears here that fast decay was necessary for ion concentration build-up in the
348 carcass, in turn responsible for the *in situ* precipitation of Fe-sulfides and Ca-phosphates replicating very
349 fine and labile details. In other words, the preservation of anatomical details required fast biologically-
350 induced decay (biodegradation). This apparent paradox implies the destruction – through biodegradation
351 – of the most labile structures within the carcass of organisms that would eventually be collected as
352 ‘exceptionally-preserved fossils’ Thus, even fast biodegradation did not allow the anatomy of the
353 investigated fossils to be preserved in its entirety, illustrating that even exceptionally preserved fossils
354 are not devoid of taphonomic biases.

356 CONCLUSIONS

357
358 1 – The early precipitation of fluorapatite and pyrite (and associated sulfides) led to exceptional
359 morphological preservation. Mg-calcite precipitated afterwards, while the sediment was still soft,
360 protecting the preserved fine anatomical details and forming the concretion.

361 2 – Mineralogy is correlated with tissue type, underlying a precursor effect, be it decay resistance or
362 local micro-environment (chemistry, microbes).

363 3 – Very early mineral precipitation, and thus, morphological replication was paradoxically fuelled by
364 fast biodegradation.

365 4 – Exceptionally preserved fossils are, when mineralized, not devoid of taphonomical bias.

366 5 – The La Voulte Lagerstätte palaeoenvironment was probably not totally anoxic, but either only very
367 locally (micro-environment) or temporarily.

Acknowledgements. We gratefully acknowledge financial support from the MNHN (ATM project Crevoulte and IntraDepartment project PerSyst), the Société des Amis du Muséum and the INSU INTERVIE program. Special thanks go to Jean-Michel Pacaud (MNHN) for access to the MNHN collections, François Loll (Structure et Instabilité des Génomes) for his help with mosaic light imaging, Nicolas Menguy (IMPMC) for his help with TEM, Corentin Le Guillou (UMET) for his help with STXM-based XANES spectroscopy, Myriam Agnel (ISTO) and Tony Appelo for their help with PHREEQC, and Elisabeth Malassis (IMPMC) and Mélinée Deretz (MNHN) for administrative simplification. We also thank David Kilcoyne (ALS – STXM Polymer beamline), Stefan Stanescu (SOLEIL – HERMES beamline) and Sufal Swaraj (SOLEIL – HERMES beamline) for STXM expert support, Solenn Réguer (SOLEIL – DiffAbs beamline) and Dominique Thiaudière (SOLEIL – DiffAbs beamline) for XRF-XRD expert support, Jean-Michel Guigner (IMPMC) for TEM expert support and Imene Estève (IMPMC) for SEM expert support. We thank SOLEIL and ALS synchrotrons for providing beamtime for the synchrotron experiments. The SEM facility at IMPMC is supported by Region Ile de France grant SESAME Number I-07-593/R, INSU-CNRS, INP-CNRS and UPMC-Paris 6, and by the Agence Nationale de la Recherche (ANR) grant number ANR-07-BLAN-0124-01. The TEM facility at IMPMC is supported by Région Ile de France grant SESAME 2000 E 1435. The STXM Polymer beamline (ALS) is supported by the Director of the Office of Science, Department of Energy, under Contract No. DE-AC02-05CH11231. The DiffAbs and HERMES beamlines (SOLEIL) are supported by the CNRS, the CEA, the Region Ile de France, the Departmental Council of Essonne and the Region Centre. The authors would like to thank Dr. James D. Schiffbauer and another anonymous reviewer for their constructive comments and questions. The editor, Dr. Robert Sansom and publications officer, Dr. Sally Thomas, are dearly thanked for their helpful comments and propositions.

References

- ALLISON, P. A. 1988. Konservat-Lagerstätten: cause and classification. *Paleobiology*, **14**, 331–344.
- APPELO, C. a J. and POSTMA, D. 2005. *Geochemistry, Groundwater and Pollution, 2nd edition*. A.A. Balkema, Leiden.

397 AUDIO, D. and SCHWEIGERT, G. 2018. Large polychelidan lobsters with a rounded carapace from
 398 the Middle Jurassic La Voulte-sur-Rhône Lagerstätte: taxonomic clarifications. *Geodiversitas*,
 399 **40**, 183–194.

400 ———, ———, SAINT MARTIN, J.-P. and CHARBONNIER, S. 2014a. High biodiversity in
 401 Polychelida crustaceans from the Jurassic La Voulte-sur-Rhône Lagerstätte. *Geodiversitas*, **36**,
 402 489–525.

403 ———, ———, HAUG, J. T., HAUG, C., SAINT MARTIN, J. P. and CHARBONNIER, S. 2014b.
 404 Diversity and palaeoecology of the enigmatic genus Knebelia (Eucrustacea, Decapoda,
 405 Eryonidae) from Upper Jurassic plattenkalks in southern Germany. *Palaeontology*, **57**, 397–416.

406 ———, HAUG, J. T., HAUG, C., CHARBONNIER, S., SCHWEIGERT, G., MÜLLER, C. H. G. and
 407 HARZSCH, S. 2016. On the sighted ancestry of blindness – exceptionally preserved eyes of
 408 Mesozoic polychelidan lobsters. *Zoological Letters*, **2**, 13.

409 ———, ROBIN, N., LUQUE, J., KROBICKI, M., HAUG, J. T., HAUG, C., JAUVION, C. and
 410 CHARBONNIER, S. 2019. Palaeoecology of Voulteryon parvulus (Eucrustacea, Polychelida)
 411 from the Middle Jurassic of La Voulte-sur-Rhône Fossil-Lagerstätte (France). *Scientific Reports*,
 412 **9**, 5332.

413 BABOLI, J., SCIENCES, P., BABOLI, M. J., VELAYATZADEH, M., BRANCH, A. and CLUB, Y.
 414 R. 2013. Determination of Heavy Metals and Trace Elements in the Muscles of Marine Shrimp ,
 415 Fenneropenaeus Merguiensis From Persian Gulf ., *Journal of Animal and Plant Sciences*, **23**,
 416 786–791.

417 BAUDELET, F., BELKHOUE, R., BRIOIS, V., COATI, A., DUMAS, P. and ET, A. 2005. Soleil a
 418 New Powerful Tool for Materials Science. *Oil & Gas Science and Technology*, **60**, 849–874.

419 BELKHOUE, R., STANESCU, S., SWARAJ, S., BESSON, A., LEDOUX, M., HAJLAOUI, M. and
 420 DALLE, D. 2015. HERMES: A soft X-ray beamline dedicated to X-ray microscopy. *Journal of*
 421 *Synchrotron Radiation*, **22**, 968–979.

422 BENZERARA, K., MENGUY, N., GUYOT, F., VANNI, C. and GILLET, P. 2005. TEM study of a
 423 silicate-carbonate-microbe interface prepared by focused ion beam milling. *Geochimica et*
 424 *Cosmochimica Acta*, **69**, 1413–1422.

425 ———, MIOT, J., MORIN, G., ONA-NGUEMA, G., SKOURI-PANET, F. and FÉRARD, C. 2011.
 426 Significance, mechanisms and environmental implications of microbial biomineralization.
 427 *Comptes Rendus - Geoscience*, **343**, 160–167.

428 BENZERARA, K., MENGUY, N., LOPEZ-GARCIA, P., YOON, T.-H., KAZMIERCZAK, J.,
 429 TYLISZCZAK, T., GUYOT, F. and BROWN, G. E. 2006. Nanoscale detection of organic
 430 signatures in carbonate microbialites. *Proceedings of the National Academy of Sciences*, **103**,
 431 9440–9445.

432 BERNARD, S., BENZERARA, K., BEYSSAC, O., MENGUY, N., GUYOT, F., BROWN JR, G. E.
 433 and GOFFE, B. 2007. Exceptional preservation of fossil plant spores in high-pressure
 434 metamorphic rocks. *Earth and Planetary Science Letters*, **262**, 257–272.

435 BLANC, P., LASSIN, A., PIAANTONE, P., AZAROUAL, M., JACQUEMET, N., FABBRI, A. and
 436 GAUCHER, E. C. 2012. Thermoddem: A geochemical database focused on low temperature
 437 water/rock interactions and waste materials. *Applied Geochemistry*, **27**, 2107–2116.

438 LE BOURLOT, C., LANDOIS, P., DJAZIRI, S., RENAULT, P.-O., LE BOURHIS, E., GOUDEAU,
 439 P., PINAULT, M., MAYNE-L'HERMITE, M., BACROIX, B., FAURIE, D., CASTELNAU, O.,
 440 LAUNOIS, P., ROUZIÈRE, S. and IUCR. 2012. Synchrotron X-ray diffraction experiments with
 441 a prototype hybrid pixel detector. *Journal of Applied Crystallography*, **45**, 38–47.

442 BRIGGS, D. E. G. and KEAR, A. J. 1993. Fossilization of soft tissue in the laboratory. *Science (New*
 443 *York, N.Y.)*, **259**, 1439–1442.

444 ——— and ———. 1994. Decay and Mineralization of Shrimps. *Palaios*, **9**, 431.

445 BRIGGS, D. E. G. and WILBY, P. R. 1996. The role of the calcium carbonate-calcium phosphate
 446 switch in the mineralization of soft-bodied fossils. *Journal of the Geological Society*, **153**, 665–
 447 668.

448 BRIGGS, D. E. G. and MCMAHON, S. 2016. The role of experiments in investigating the taphonomy
 449 of exceptional preservation. *Palaeontology*, **59**, 1–11.

450 BRIGGS, D. E. G., KEAR, A. J., MARTILL, D. M. and WILBY, P. R. 1993. Phosphatization of soft-
 451 tissue in experiments and fossils. *Journal of the Geological Society*, **150**, 1035–1038.

452 BRODA, K., HEGNA, T. A. and ZATON, M. 2015. Thylacocephalans. *Geology Today*, **31**, 116–120.

453 CASENOVE, D., OJI, T. and GOTO, T. 2011. Experimental Taphonomy of Benthic Chaetognaths:
 454 Implications for the Decay Process of Paleozoic Chaetognath Fossils. *Paleontological Research*,
 455 **15**, 146–153.

456 CECCALDI, H. J. 1994. Appareil digestif : anatomie et physiologie. In GRASSÉ, P. P. (ed.) *Traité de*
 457 *Zoologie, Anatomie, Systématique, Biologie. Tome VII, Fascicule 1 : Crustacés : Morphologie,*
 458 *Physiologie, Reproduction, Embryologie.*, Masson, Paris, 487–527 pp.

459 CHARBONNIER, S. 2009. *Un environnement bathyal au Jurassique : le Lagerstätte de La Voulte.*
 460 Mémoires du Muséum national d'Histoire naturelle.

461 CHARBONNIER, S., VANNIER, J. and RIOU, B. 2007a. New sea spiders from the Jurassic La
 462 Voulte-sur-Rhône Lagerstätte. *Proceedings. Biological sciences / The Royal Society*, **274**, 2555–
 463 61.

464 CHARBONNIER, S., VANNIER, J., HANTZPERGUE, P. and GAILLARD, C. 2010. Ecological
 465 Significance of the Arthropod Fauna from the Jurassic (Callovian) La Voulte Lagerstätte. *Acta*
 466 *Palaeontologica Polonica*, **55**, 111–132.

467 ———, AUDO, D., CAZE, B. and BIOT, V. 2014. The La Voulte-sur-Rhône Lagerstätte (Middle
 468 Jurassic, France). *Comptes Rendus - Palevol*, **13**, 369–381.

469 ———, VANNIER, J., GAILLARD, C., BOURSEAU, J.-P. and HANTZPERGUE, P. 2007b. The La
 470 Voulte Lagerstätte (Callovian): Evidence for a deep water setting from sponge and crinoid
 471 communities. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **250**, 216–236.

472 ———, TERUZZI, G., AUDO, D., LASSERON, M., HAUG, C. and HAUG, J. T. 2017. New
 473 thylacocephalans from the Cretaceous Lagerstätten of Lebanon. *Bulletin de la Société géologique*
 474 *de France*, **188**, 19.

475 COOK, P. K., MOCUTA, C., DUFOUR, É., LANGUILLE, M.-A. and BERTRAND, L. 2018. Full-
 476 section otolith microtexture imaged by local-probe X-ray diffraction. *Journal of Applied*
 477 *Crystallography*, **51**, 1182–1196.

478 COSMIDIS, J. and BENZERARA, K. 2014. Soft x-ray scanning transmission spectromicroscopy. In
 479 DIMASI, E. and GOWER, L. B. (eds.) *Biom mineralization Sourcebook - Characterization of*
 480 *Biom minerals and Biomimetic Materials*, CRC Press, Taylor and Francis Group, Boca Raton, 432

481 pp.

482 ———, ———, GUYOT, F., SKOURI-PANET, F., DUPRAT, E., GUIGNER, J.-M.,

483 BABONNEAU, F. and COELHO, C. 2015. Calcium-Phosphate Biomineralization Induced by

484 Alkaline Phosphatase Activity in *Escherichia coli* : Localization , Kinetics , and Potential

485 Signatures in the Fossil Record. *Frontiers in Earth Science*, **3**, 1–20.

486 ———, ———, MORIN, G., BUSIGNY, V., LEBEAU, O., JÉZÉQUEL, D., NOËL, V., DUBLET,

487 G. and OTHMANE, G. 2014. Biomineralization of iron-phosphates in the water column of Lake

488 Pavin (Massif Central, France). *Geochimica et Cosmochimica Acta*, **126**, 78–96.

489 CURTIS, C. 1987. Mineralogical Consequences of Organic Matter Degradation in Sediments:

490 Inorganic/Organic Diagenesis. *Marine clastic sedimentology*, **Chapter 6**, 108–123.

491 DELPIERRE, P., BASOLO, S., BERAR, J. F., BORDESOULE, M., BOUDET, N., BREUGNON, P.,

492 CAILLOT, B., CHANTEPIE, B., CLEMENS, J. C., DINKESPILER, B., HUSTACHE-OTTINI,

493 S., MEESSEN, C., MENOUNI, M., MOREL, C., MOUGET, C., PANGAUD, P., POTHEAU, R.

494 and VIGEOLAS, E. 2007. XPAD: A photons counting pixel detector for material sciences and

495 small-animal imaging. *Nuclear Instruments and Methods in Physics Research, Section A:*

496 *Accelerators, Spectrometers, Detectors and Associated Equipment*, **572**, 250–253.

497 ELMI, S. 1990a. Stages in the evolution of late Triassic and Jurassic carbonate platforms: the western

498 margin of the Subalpine Basin (Ardèche, France). In TUCKER, M. E. (ed.) *Carbonate*

499 *Platforms, Facies, Sequences and Evolution. Special Publication Number 9 of the International*

500 *Association of Sedimentologists.*, Blackwell Scientific Publications, 109–144 pp.

501 ———. 1990b. Les applications géodynamiques de la stratigraphie: l’histoire triasico-jurasique de la

502 marge vivaro-cévenole France, Sud-Est). *Documents des Laboratoires de Géologie de la Faculté*

503 *des Sciences de Lyon*, **hors série**, 93–123.

504 ESTEVE, M. and HERRERA, F. C. 2000. Hepatopancreatic alterations in *Litopenaeus vannamei*

505 (Boone, 1939) (Crustacea: Decapoda: Penaeidae) experimentally infected with a *Vibrio*

506 *alginolyticus* strain. *Journal of invertebrate pathology*, **76**, 1–5.

507 FISCHER, J.-C. 2003. Invertébrés remarquables du Callovien inférieur de la Voulte-sur-Rhône

508 (Ardèche, France). *Annales de Paléontologie*, **89**, 223–252.

509 ——— and RIOU, B. 1982. Les teuthoïdes (Cephalopoda, Dibranchiata) du callovien inférieur de la
510 Voulte-sur-Rhône (Ardèche, France). *Annales de Paléontologie*, **68**, 295–325.

511 FISCHER, J. C. and RIOU, B. 2002. Vampyronassa rhodanica nov. gen. nov sp., vampyromorphe
512 (Cephalopoda, Coleoidea) Du Callovien inférieur de la Voulte-sur-Rhône (Ardèche, France).
513 *Annales de Paleontologie*, **88**, 1–17.

514 FÖLLMI, K. B. 1996. The phosphorus cycle , phosphogenesis and marine phosphate-rich deposits.
515 *Earth-Science Reviews*, **40**, 55–124.

516 GUERIAU, P., JAUVION, C. and MOCUTA, C. 2018. Show me your yttrium, and I will tell you who
517 you are: implications for fossil imaging. *Palaeontology*, **61**, 981–990.

518 HAUG, C., BRIGGS, D. E. G., MIKULIC, D. G., KLUESSENDORF, J. and HAUG, J. T. 2014. The
519 implications of a Silurian and other thylacocephalan crustaceans for the functional morphology
520 and systematic affinities of the group. *BMC Evolutionary Biology*, **14**, 159.

521 HOF, C. H. J. and BRIGGS, D. E. G. 1997. Decay and Mineralization of Mantis Shrimps
522 (Stomatopoda: Crustacea) - A Key to Their Fossil Record. *PALAIOS*, **12**, 420–438.

523 ICELY, J. and NOTT, J. A. 1992. Digestion and absorption: digestive system and associated organs.
524 In HARRISON, F. W. and HUMES, A. G. (eds.) *Microscopic Anatomy of Invertebrates*,
525 *Decapod Crustacea. Vol. 10.*, Wiley-Liss Inc, New York, 147–201 pp.

526 INIESTO, M., LOPEZ-ARCHILLA, A. I., FRENÉGAL-MARTINEZ, M., BUSCALIONI, A. D. and
527 GUERRERO, M. C. 2013. Involvement of Microbial Mats in Delayed Decay: an Experimental
528 Essay on Fish Preservation. *Palaaios*, **28**, 56–66.

529 INIESTO, M., BUSCALIONI, Á. D., CARMEN GUERRERO, M., BENZERARA, K., MOREIRA,
530 D. and LÓPEZ-ARCHILLA, A. I. 2016. Involvement of microbial mats in early fossilization by
531 decay delay and formation of impressions and replicas of vertebrates and invertebrates. *Scientific*
532 *Reports*, **6**, 25716.

533 ———, ZEYEN, N., LÓPEZ-ARCHILLA, A. I., BERNARD, S., BUSCALIONI, Á. D.,
534 GUERRERO, M. C. and BENZERARA, K. 2015. Preservation in microbial mats: mineralization
535 by a talc-like phase of a fish embedded in a microbial sarcophagus. *Frontiers in Earth Science*, **3**,
536 51.

537 IO, E. and HA, F. 2013. Proximate and Mineral Compositions of Common Crab Species [*Callinectes*
 538 *pallidus* and *Cardisoma armatum*] of Badagry Creek, Nigeria. *Poultry, Fisheries and Wildlife*
 539 *Sciences*, **2**, 1–5.

540 JAUUVION, C., CHARBONNIER, S. and BERNARD, S. 2017. A new look at the shrimps (Crustacea ,
 541 Decapoda , Penaeoidea) from the Middle Jurassic La Voulte-sur-Rhône Lagerstätte.
 542 *Geodiversitas*, **39**, 705–716.

543 ———, AUDIO, D., CHARBONNIER, S. and VANNIER, J. 2016. Virtual dissection and lifestyle of
 544 a 165 million-year-old female polychelidan lobster. *Arthropod Structure & Development*, **45**,
 545 122–132.

546 KIDWELL, S. M. and FLESSA, K. W. 1995. THE QUALITY OF THE FOSSIL RECORD:
 547 Populations, Species, and Communities. *Annu. Rev. Ecol. Syst.*, **26**, 269–299.

548 KILCOYNE, A. L. D., TYLISZCZAK, T., STEELE, W. F., FAKRA, S., HITCHCOCK, P.,
 549 FRANCK, K., ANDERSON, E., HARTENECK, B., RIGHTOR, E. G., MITCHELL, G. E.,
 550 HITCHCOCK, A. P., YANG, L., WARWICK, T. and ADE, H. 2003. Interferometer-controlled
 551 scanning transmission X-ray microscopes at the Advanced Light Source. *Journal of Synchrotron*
 552 *Radiation*, **10**, 125–136.

553 KIRKPATRICK, P. and BAEZ, A. V. V. 1948. Formation of Optical Images by X-Rays. *Journal of*
 554 *the Optical Society of America*, **38**, 766.

555 KRUTA, I., ROUGET, I., CHARBONNIER, S., BARDIN, J., FERNANDEZ, V., GERMAIN, D.,
 556 BRAYARD, A. and LANDMAN, N. 2016. Proteroctopus ribeti in coleoid evolution.
 557 *Palaeontology*, **59**, 767–773.

558 LANGE, S., SCHRAM, F. R., STEEMAN, F. A. and HOF, C. H. J. 2001. New genus and species
 559 from the cretaceous of Lebanon links the thylacocephala to the crustacea. *Palaeontology*, **44**,
 560 905–912.

561 LECLERCQ, N., POIRIER, S., LÊ, S., LANGLOIS, F., MEDJOUBI, K., BLACHE, F., BISOU, J.
 562 and MOCUTA, C. 2015. FLYSCAN: A Fast and Multi-Technique Data Acquisition Platform for
 563 the SOLEIL Beamlines. .

564 LEPOT, K., BENZERARA, K., BROWN, G. E. and PHILIPPOT, P. 2008. Microbially influenced

565 formation of 2,724-million-year-old stromatolites. *Nature Geoscience*, **1**, 118–121.

566 MAYRAT, A. 1994. Appareil circulatoire. In GRASSÉ, P. P. (ed.) *Traité de Zoologie, Anatomie,*
567 *Systématique, Biologie. Tome VII, Fascicule 1 : Crustacés : Morphologie, Physiologie,*
568 *Reproduction, Embryologie.*, Masson, Paris, 435–485 pp.

569 MEDJOUBI, K., BUCAILLE, T., HUSTACHE, S., BÉRAR, J.-F., BOUDET, N., CLEMENS, J.-C.,
570 DELPIERRE, P. and DINKESPILER, B. 2010. Detective quantum efficiency, modulation
571 transfer function and energy resolution comparison between CdTe and silicon sensors bump-
572 bonded to XPAD3S. *Journal of Synchrotron Radiation*, **17**, 486–495.

573 MIOT, J., JÉZÉQUEL, D., BENZERARA, K., CORDIER, L., RIVAS-LAMELO, S., SKOURI-
574 PANET, F., FÉRARD, C., POINSOT, M. and DUPRAT, E. 2016. Mineralogical Diversity in
575 Lake Pavin : Connections with Water Column Chemistry and Biomineralization Processes.
576 *Minerals*, **6**, 1–19.

577 MOCUTA, C., RICHARD, M.-I., FOUET, J., STANESCU, S., BARBIER, A., GUICHET, C.,
578 THOMAS, O., HUSTACHE, S., ZOZULYA, A. V., THIAUDIÈRE, D. and IUCR. 2013. Fast
579 pole figure acquisition using area detectors at the DiffAbs beamline – Synchrotron SOLEIL.
580 *Journal of Applied Crystallography*, **46**, 1842–1853.

581 MOREAU, J. W., WEBB, R. I. and BANFIELD, J. F. 2004. Ultrastructure, aggregation-state, and
582 crystal growth of the biogenic nanocrystalline sphalerite and wurtzite. *American Mineralogist*,
583 **89**, 950–960.

584 MURDOCK, D. J., GABBOTT, S. E., MAYER, G. and PURNELL, M. a. 2014. Decay of velvet
585 worms (Onychophora), and bias in the fossil record of lobopodians. *BMC Evolutionary Biology*,
586 **14**.

587 MUSCENTE, A. D., SCHIFFBAUER, J. D., BROCE, J., LAFLAMME, M., O'DONNELL, K.,
588 BOAG, T. H., MEYER, M., HAWKINS, A. D., HUNTLEY, J. W., MCNAMARA, M.,
589 MACKENZIE, L. A., STANLEY, G. D., HINMAN, N. W., HOFMANN, M. H. and XIAO, S.
590 2017. Exceptionally preserved fossil assemblages through geologic time and space. *Gondwana*
591 *Research*, **48**, 164–188.

592 PARKHURST, D. L. and APPELO, C. A. J. 2013. Description of input and examples for PHREEQC

version 3--A computer program for speciation, batch-reaction, one-dimensional transport, and
inverse geochemical calculations. **book 6**, 497.

PARRY, L. A., SMITHWICK, F., NORDÉN, K. K., SAITTA, E. T., LOZANO-FERNANDEZ, J.,
TANNER, A. R., CARON, J. B., EDGECOMBE, G. D., BRIGGS, D. E. G. and VINTHER, J.
2018. Soft-Bodied Fossils Are Not Simply Rotten Carcasses – Toward a Holistic Understanding
of Exceptional Fossil Preservation: Exceptional Fossil Preservation Is Complex and Involves the
Interplay of Numerous Biological and Geological Processes. *BioEssays*, **40**, 1–11.

PERRIER, V. and CHARBONNIER, S. 2014. The Montceau-les-Mines Lagerstätte (Late
Carboniferous, France). *Comptes Rendus Palevol*, **13**, 353–367.

PINNA, G., ARDUINI, P., PESARINI, C. and TERUZZI, G. 1982. Thylacocephala: una nuova classe
di crostacei fossili. *Atti della Societa italiana di Scienze naturali e del Museo civico di Storia
naturale di Milano*, **123**, 469–482.

POURANG, N. and AMINI, G. 2001. DISTRIBUTION OF TRACE ELEMENTS IN TISSUES OF
TWO SHRIMP SPECIES FROM PERSIAN GULF AND EFFECTS OF STORAGE
TEMPERATURE ON ELEMENTS TRANSPORTATION. *Water, Air, and Soil Pollution*, **129**,
229–243.

PRATT, B. R. and KIMMIG, J. 2019. Extensive bioturbation in a middle Cambrian Burgess Shale–
type fossil Lagerstätte in northwestern Canada. *Geology*, **47**, 1–4.

PURNELL, M. A., DONOGHUE, P. J. C., GABBOTT, S. E., MCNAMARA, M. E., MURDOCK, D.
J. E. and SANSOM, R. S. 2018. Experimental analysis of soft-tissue fossilization: opening the
black box. *Palaeontology*, **61**, 317–323.

RAFF, E. C., ANDREWS, M. E., TURNER, F. R., TOH, E., NELSON, D. E. and RAFF, R. A. 2013.
Contingent interactions among biofilm-forming bacteria determine preservation or decay in the
first steps toward fossilization of marine embryos. *Evolution and Development*, **15**.

RAFF, R. A., ANDREWS, M. E., PEARSON, R. L., TURNER, F. R., SAUR, S. T., THOMAS, D. C.,
EAGAN, J. L. and RAFF, E. C. 2014. MICROBIAL ECOLOGY AND BIOFILMS IN THE
TAPHONOMY OF SOFT TISSUES. *PALAIOS*, **29**, 560–569.

RAISWELL, R. 1993. Kinetic controls on depth variations in localised pyrite formation. *Chemical*

621 *Geology*, **107**, 467–469.

622 RAISWELL, R., WHALER, K., DEAN, S., COLEMAN, M. . and BRIGGS, D. E. . 1993. A simple
623 three-dimensional model of diffusion-with-precipitation applied to localised pyrite formation in
624 framboids, fossils and detrital iron minerals. *Marine Geology*, **113**, 89–100.

625 RAVEL, B. and NEWVILLE, M. 2005. ATHENA, ARTEMIS, HEPHAESTUS: Data analysis for X-
626 ray absorption spectroscopy using IFEFFIT. *Journal of Synchrotron Radiation*, **12**, 537–541.

627 SAGEMANN, J., BALE, S. J., BRIGGS, D. E. . and PARKES, R. J. J. 1999. Controls on the
628 formation of authigenic minerals in association with decaying organic matter: An experimental
629 approach. *Geochimica et Cosmochimica Acta*, **63**, 1083–1095.

630 SANSOM, R. S. 2016. Preservation and phylogeny of Cambrian ecdysozoans tested by experimental
631 decay of Priapulid. *Scientific Reports*, **6**, 1–12.

632 ———, GABBOTT, S. E. and PURNELL, M. A. 2010. Non-random decay of chordate characters
633 causes bias in fossil interpretation. *Nature*, **463**, 797–800.

634 SANSOM, R. S., GABBOTT, S. E. and PURNELL, M. A. 2011. Decay of vertebrate characters in
635 hagfish and lamprey (Cyclostomata) and the implications for the vertebrate fossil record.
636 *Proceedings of the Royal Society B: Biological Sciences*, **278**, 1150–1157.

637 SANSOM, R. S., GABBOTT, S. E. and PURNELL, M. A. 2013. Atlas of vertebrate decay: A visual
638 and taphonomic guide to fossil interpretation. *Palaeontology*, **56**, 457–474.

639 SCHIFFBAUER, J. D., WALLACE, A. F., BROCE, J. and XIAO, S. 2014. Exceptional fossil
640 conservation through phosphatization. *Paleontological Society Papers*, **20**, 59–82.

641 SCHRAM, F. R. 2014. Family level classification within thylacocephala, with comments on their
642 evolution and possible relationships. *Crustaceana*, **87**, 340–363.

643 ———, HOF, C. H. J. and STEEMAN, F. A. 1999. Thylacocephala (Arthropoda: Crustacea ?) from
644 the Cretaceous of Lebanon and Implications for Thylacocephalan Systematics. *Palaeontology*,
645 **42**, 769–797.

646 SECRETAN, S. 1983. Une nouvelle classe fossile dans la super-classe des Crustacés :
647 Conchyliocarida. *Comptes rendus de l'Academie des Sciences Serie II, Fascicule A, Sciences de*
648 *la Terre et des Planètes*, **296**, 741–743.

649 ———. 1985. Conchyliocarida, a class of fossil crustaceans: relationships to Malacostraca and
 650 postulated behaviour. *Transactions of the Royal Society of Edinburgh: Earth Sciences*, **76**, 381–
 651 389.

652 ——— and RIOU, B. 1983. Un groupe énigmatique de crustacés: ses représentants du Callovien de la
 653 Voulte-sur-Rhône. *Annales de paléontologie (Vertébrés-Invertébrés)*, **69**, 59–97.

654 SEILACHER, A. 1970. Begriff und Bedeutung der Fossil-Lagerstätten. *Neues Jahrbuch für Geologie*
 655 *und Paläontologie - Monatshefte*, 34–39.

656 VAN STRAELEN, V. 1923. Les Mysidacés du Callovien de La Voulte-sur-Rhône (Ardèche).
 657 *Bulletin de la Société Géologique de France*, **23**, 431–439.

658 SWARAJ, S., BELKHOU, R., STANESCU, S., RIOULT, M., BESSON, A. and HITCHCOCK, A. P.
 659 2017. Performance of the HERMES beamline at the carbon K-edge. *Journal of Physics:*
 660 *Conference Series*, **849**.

661 VANNIER, J., CHEN, J. U. N. Y., HUANG, D. I. Y., CHARBONNIER, S. and WANG, X. I. U. Q.
 662 2006. The Early Cambrian origin of thylacocephalan arthropods. *Acta Palaeontologica Polonica*,
 663 **51**, 201–214.

664 ———, SCHOENEMANN, B., GILLOT, T., CHARBONNIER, S. and CLARKSON, E. 2016.
 665 Exceptional preservation of eye structure in arthropod visual predators from the Middle Jurassic.
 666 *Nature Communications*, **7**, 10320.

667 WILBY, P. R., BRIGGS, D. E. G. and RIOU, B. 1996. Mineralization of soft-bodied invertebrates in a
 668 Jurassic metalliferous deposit. *Geology*, **24**, 847–850.

669 WILSON, P., PARRY, L. A., VINTHER, J. and EDGECOMBE, G. D. 2016. Unveiling biases in soft-
 670 tissue phosphatization: Extensive preservation of musculature in the Cretaceous (Cenomanian)
 671 polychaete *Rollinschaeta myoplana* (Annelida: Amphinomidae). *Palaeontology*, **59**, 463–479.

672 XIAO, S. and SCHIFFBAUER, J. D. 2009. Microfossil phosphatization and its astrobiological
 673 implications. In *From Fossils to Astrobiology*, Springer, 89–117 pp.

674 ZOUGROU, I. M., KATSIKINI, M., PINAKIDOU, F., BRZHEZINSKAYA, M.,
 675 PAPADOPOULOU, L., VLACHOS, E., TSOUKALA, E. and PALOURA, E. C. 2016.
 676 Characterization of fossil remains using XRF, XPS and XAFS spectroscopies. *Journal of*

677 *Physics: Conference Series*, **712**.

678

679

Figure captions and tables with captions

FIG. 1. Location of the La Voulte Lagerstätte. A, Site location and geological context; B, Photograph of specimen FSL 710064 of *Dollocaris ingens*, right lateral view; C, Reconstruction of *D. ingens* by Secretan (1985), right lateral view. ai, antero-inferior spine, ap, appendage, dm, dorsal margin, mdr, medio-dorsal ridge, o, eye, r, rostrum, vm, ventral margin. Photograph: B, S. Charbonnier. Scale bars are 500 m in A and 5 mm in B. **[Intended for single-column width].**

FIG. 2. Internal anatomy of investigated specimens of *Dollocaris ingens*. A, schematic of the approximate positions of each section; B, unpolished section of specimen MNHN.F.A66910, photograph; C, polished section of specimen MNHN.F.R06054; D, thin section of specimen MNHN.F.A70115, cross polarized light. c, cuticle, g, gills, h, heart, hv, hemolymphatic vessels hp, hepatopancreas (digestive gland), m, muscles, mf, muscular fibres, mx, sedimentary matrix, st, stomach, v, valve. Images: B, P. Gueriau; C, S. Charbonnier, polished section by S. Secrétan; D, F. Loll. Scale bars are 5 mm in B–C and 10 mm in D. **[Intended for full page width].**

FIG. 3. Mineral phases (optical microscopy) of a thin section of specimen MNHN.F.A70115 (*Dollocaris ingens*). A, Detail of the heart and gills, cross polarized light; B, details of muscular fibres, cross polarized light; C, crystal morphology and chronology, direction of crystal growth is clear (arrow), beginning on a layered structure of probable organic origin, cross polarized light. ap, apatite, ca, calcite, g, gills, h, heart, mf, muscular fibres, py, pyrite (see text and Fig. 6A later on for details). Scale bars are 500 mm in A, 200 mm in B and 100 mm in C. **[Intended for single-column page width].**

FIG. 4. Elemental maps (SEM-EDX) of two areas of a polished section of specimen MNHN.F.R06054.03 (A–B and D–E) and of an area of a thin section of specimen MNHN.F. A70114 (C, F) and corresponding EDX spectra. A and D, SEM-EDX elemental maps of a detail of the heart (h); B and E, SEM-EDX elemental map of a detail of the hepatopancreas (hp) and valve (v); C and F, SEM-EDX elemental map of a reaction front at the contact between the detrital infill (bottom) and the early

mineral phases (top); G, EDX spectra of the main mineral phases encountered in investigated specimens (see text and Fig. 6A later on for details). Scales bars are 200 μm in A–B and 40 μm in C. **[Intended for full page width].**

FIG. 5. Heavy element (atomic number $Z \geq 20$) distribution (XRF maps) in polished sections of specimens MNHN.F.A66910 (A–B) and MNHN.F.R06054.03 (C–D) of *Dollocaris ingens*. Y and Sr are trace elements in carbonates and phosphates, Y being richer in phosphates than carbonates (see Gueriau et al., 2018 for discussion); Zn is constitutive of Zn-sulfides, such as wurtzite; Pb is present in trace amounts in Fe-sulfides and is constitutive of Pb-sulfides (galena). Rb is present in trace amounts in silicate detrital material. Mn is present in trace amounts in carbonates. c, cuticle, g, gills, h, heart, hv, hemolymphatic vessels hp, hepatopancreas (digestive gland), m, muscles, mx, sedimentary matrix, v, valve. Scale bars are 5 mm. **[Intended for full page width].**

FIG. 6. Mineralogical composition and distribution of investigated specimens of *Dollocaris ingens* (XRD). A, Synchrotron-based diffractograms of the entire sections of specimens MNHN.F.A66910 and MNHN.F.R06054.03 (2θ recalculated from synchrotron energy, 18–18.2 keV) and powder diffractograms of various parts/organs of specimen MNHN.F.A66910. a, argentopyrite; $\bar{a}$, arsenopyrite; c, magnesian calcite; d, dolomite; e, epsomite; h, halloysite-7 Å; i, illite; o, opal-CT (indicated by cristobalite or tridymite); p, apatite; pe?, pentlandite (uncertain); sh, shortite; w, wurtzite; y, pyrrhotite; β , cristobalite beta; π , pyrite. Mineralogical distribution (XRD maps) in polished sections of specimens MNHN.F.A66910 (B–C) and MNHN.F.R06054.03 (D). apat, apatite, aspy, arsenopyrite, calc, magnesian calcite, opal, opal-CT (peak attributed to cristobalite or tridymite) pyri, pyrite, pyrr, pyrrhotite, wurt, wurtzite. c, cuticle, g, gills, h, heart, hv, hemolymphatic vessels hp, hepatopancreas (digestive gland), m, muscles, mx, sedimentary matrix, v, valve. Scale bars are 5 mm. **[Intended for full page width].**

FIG. 7. Fine-scale mineral identification. Ca $L_{2,3}$ -edge XANES spectroscopy (A) and STEM images (B–C) of FIB foils extracted from a thin section of specimen MNHN.F. A70114. Pyrite (see B) and apatite

(see C) are automorphic in contrast to Mg-calcite (see B). ap, apatite; ca, magnesian calcite; py, pyrite.
Scale bars are 1 μm in B and 100 nm in C. **[Intended for full page width].**

FIG. 8. PHREEQC-based estimations of mineral precipitation as a function of temperature (at 20 bars, see text for details). **[Intended for full page width].**

FIG. 9. PHREEQC-based estimations of mineral precipitation, pH and pE as a function of pore volume cycles (steps) in the advective-diffusive oxidation model (see text for detail). **[Intended for full page width].**

FIG. 10. Exceptional preservation pathway for the La Voulte-sur-Rhône Lagerstätte. **[Intended for full page width].**

TABLE 1. Initial model water composition.

TABLE 2. Tissue and organ summarized mineralogical composition. (*Lumen is not a tissue type*).

TABLE 3. Tissue-specific elemental composition of modern crustaceans (compilation, see text) [intended for landscape format]

A

B

C

Early Diagenesis

**Exceptional
Preservation**

**Cementation
Nodule formation**

Death

*Anaerobic decay
(Sulfate-reducing Bacteria)*

Fluorapatite + Pyrite (and other sulfides) precipitation

Decay continues

*system 'opens'
pH increases*

Mg-calcite precipitation

Sediment intrusion

Local oxidation

Pyrite + Mg-calcite → Fe-oxides + Mg-sulfates

Lithification

Fossil discovery

Late Diagenesis