# Significance of partial leaching in calcareous ooids: The case study of Hauterivian oolites in Switzerland

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**Abstract:** In the Canton of Vaud (Switzerland), two Hauterivian oolitic units were penetrated by a borehole. In both units, the ooids are partly leached. More specifically, the ooid cortices were partly leached and some ooid nuclei appear suspended in the middle of cortical moldic cavities created by leaching, rather than having fallen to the bottom of these cavities before the final cementation take place. We demonstrate that these ooids were originally calcitic, not aragonitic, not "two-phase" nor "bimineral". This leaching is not an early diagenetic feature related to subaerial exposure, but a late diagenetic feature, possibly related to the migration of acidic pore waters, brought about by Alpine tectonics and/or karstification.

**Key Words:** Switzerland; Urgonian; Hauterivian; calcareous ooids; dissolution; calcite, aragonite; organic matter.

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Résumé: De l'importance des dissolutions partielles dans des ooïdes calcaires: Exemple des oolithes hauteriviennes de Suisse. Dans le Canton de Vaud (Suisse), deux unités oolithiques hauteriviennes ont été traversées par un forage. Dans ces deux unités, les ooïdes sont partiellement dissouts. Plus précisément, les cortex oolithiques ont été partiellement dissouts et quelques nuclei oolithiques semblent suspendus au milieu de cavités moldiques créées par la dissolution de ces cortex, au lieu d'être tombés sur le fond de ces mêmes cavités avant que la phase finale de cimentation ait eu lieu. Nous démontrons que ces ooïdes étaient originellement calcitiques et non aragonitiques, non composés des deux polymorphes du carbonate de calcium et encore moins de deux minéraux distincts. Cette dissolution n'est pas un phénomène diagénétique précoce lié à une émersion, mais un phénomène diagénétique tardif qui pourrait bien être lié à la circulation d'eaux souterraines acides favorisée par des réseaux de fractures (en liaison avec la structuration des Alpes) ou de conduits karstiques.

 $\textbf{Mots-clefs:} \ \text{Suisse} \ ; \ \text{Urgonien:} \ ; \ \text{Hauterivien:} \ ; \ \text{oo\"ides calcaires:} \ ; \ \text{dissolution:} \ ; \ \text{calcite:} \ ; \ \text{aragonite:} \ ; \ \text{mattière organique.}$ 

## I - Introduction

Calcareous ooids are coated grains of diverse size, shape, fabric and mineralogy (calcite and aragonite), which form one of the most fascinating category for people studying carbonate rocks. Among the special fabrics, ooids with partly replaced or dissolved cortices are commonly interpreted as "two-phase" or "bimineralic" (Tucker, 1984; Heydarl & Moore, 1994; Algeo & Watson, 1995; Chow & James, 1995). The radial-fibrous fabric of some cortical layers is considered to be primary and their original mineralogy is commonly high-Mg calcite in marine environments. In the case of a replacement, the original structures are "often obliterated and at best represented only by

faint relics" (TUCKER, 1984); this fabric is interpreted as reflecting an original aragonitic mineralogy. Similarly, in the case of dissolution (followed or not by drusy calcite cementation), the original mineralogy of these leached layers is commonly interpreted as aragonite (e.g., ZEN et al., 1983). However, in this case study, it is demonstrated that leaching has affected cortical layers with a radial-fibrous fabric and that this diagenetic pattern was not related to an original aragonitic mineralogy. Furthermore, this case demonstrates that the presence of "shrunken", "half moon" or "collapsed" ooids may not necessarily be indicative of early subaerial exposure and subsequent freshwater leaching to create secondary porosity as is commonly thought (e.g., ZEN et al., 1983). In short,

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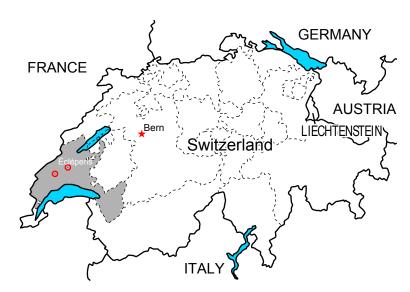
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calcareous ooids can provide useful information in terms of the environment of deposition and diagenesis (Strasser, 1986; Tucker, 2001, inter alia). The purpose of this study is to describe the petrography of distinctive ooids with partly dissolved cortices and to offer an explanation for their origin.

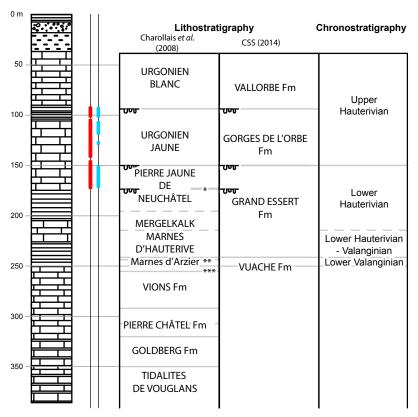
## II - Geological setting

The case studied is documented by material from a drill-hole core near Montricher (Fig. 1), a Swiss locality not far from Éclépens (less than 20 km to the east), which is better known for the controversial bio- and sequence stratigraphies of its Lower Cretaceous (Urgonian) section (see discussions in Conrad et al., 2012; Charollais et al., 2013; Granier et al., 2014). The same features can be observed in the oolitic intervals of both localities.

The Morand drill hole was initially bored in 1968 to help characterize the hydrogeological conditions and later geothermal setting of the Municipality of Montricher, District of Morges, Canton of Vaud, Switzerland. After cutting nearly 37 metres of Quaternary sediments it penetrated Lower Cretaceous strata and ended in uppermost Jurassic rocks at a depth of nearly 388 metres (MOR-NOD, 1969, unpublished; LOOSER & DAVIT, 1993; WILHELM et al., 2003; Granier et al., 2014). It was fully cored and the remaining core material is currently stored in the "Musée cantonal de Géologie" of Lausanne, Switzerland. Regarding its lithostratigraphic subdivision (Fig. 2), as in a previous paper describing the palaeophycological assemblages of the Lower Cretaceous (GRANIER et al., 2014), the regional lithostratigraphic classification proposed by Charollais et al. (2008) is adopted [in parallel we use the most recent lithostratigraphic classification of the Comité Suisse de Stratigraphie (2014)]. However with respect to the topic of interest, the focus here is on the first 200 metres of the section that spans from top to bottom:



**Figure 1:** Location map of Montricher (geographic coordinates x:520,025 y:162,180 altitude 665 m, 46°36'11.8"N 6°23'57.9"E; Google coordinates: 46.603478, 6.399386) and Éclépens (Holcim quarry, geographic coordinates x:531,256 y:167,183, 46°39'12.6"N 6°32'40.3"E; Google coordinates: 46.653485, 6.544517), Canton of Vaud, Switzerland.



**Figure 2:** Stratigraphic column of the Morand drill hole with the location of the bored hardgrounds and occurrences of the Hauterivian ooids (in red), including those with partly dissolved cortices (in blue). Lithostratigraphic log of the Morand drilling (redrawn and modified from WILHELM *et al.*, 2003, p. 130). Caption: \*: "Marnes d'Uttins", \*\*: "Calcaires roux", \*\*\*: Chambotte Fm.

- the Vallorbe Formation, formerly know as "Urgonien blanc" auct. (white Urgonian), corresponding to the interval 37.20 to 92.42 m and ascribed a Late Hauterivian age. At 92.42 m a bored hardground (Fig. 3.B-C) marks the lower boundary of this unit. In the neighbouring Éclépens section, it is thinner and eroded at its top (CONRAD et al., 2012; CHAROLLAIS et al., 2013);
- the Gorges de l'Orbe Formation, formerly know as "Urgonien jaune" auct. (yellow Urgonian), spanning the interval 92.42 to 149.30 m and also ascribed to the Late Hauterivian. At 149.30 m a bored hardground (Fig. 3.E) marks the lower boundary of the Urgonian. In the Éclépens section, this unit is nearly 50 m thick (GODET, 2006; CONRAD et al., 2012; CHAROLLAIS et al., 2013); there too a bored hardground (GODET, 2006: p. 50, Fig. B.11/D: 34 m) marks the lower boundary of the Urgonian. It is the first oolitic unit encountered downhole;
- the Grand Essert Formation, which spans the former "Pierre jaune" auct. to the former "Marnes d'Hauterive" auct. interval. The "Pierre jaune" auct. (yellow Stone) corresponds to the interval 149.30 to 195.00 m and is mostly referred to an Early Hauterivian age. It is divided into two parts, i.e., respectively the upper and the lower "Pierre jaune", separated by a bored rdground (Fig. 3.A) at 172.45 m. The upper "Pierre jaune" is the second oolitic unit encountered downhole. In the Éclépens section, this subunit is nearly 25 m thick (GODET, 2006; CONRAD et al., 2012; CHAROLLAIS et al., 2013); there, too, a bored hardground (GODET, 2006: p. 50, Fig. B.11/B-C: 8 m) marks the boundary of the two subunits. The lower "Pierre jaune" gradually passes downward to the "Mergelkalk Zone" auct. from 195.00 m that in turn passes to the "Marnes d'Hauterive" auct. (Hauterive Marls) from 216.40 m. As in the Éclépens section (CONRAD et al., 2012; CHAROLLAIS et al., 2013), the Lower -Upper Hauterivian transition is to be found in the upper "Pierre jaune" whereas the the Valanginian - Hauterivian transition is to be found in the "Marnes d'Hauterive";
- the Vuache Formation, formerly know as "Calcaires roux" auct. (red Limestones), and older units start below a stylolitic joint at 240.90 m.

People working in the same Swiss Jura area, mostly PhD students (BLANC-ALÉTRU, 1995; CARRIO-SCHAFFHAUSER, 2005; GODET *et al.*, 2005; GODET, 2006), had already reported the occurrence of ooids with partly dissolved cortices (CARRIO-SCHAFFHAUSER, 2005: p. 73, Pl. 36; GODET *et al.*, 2005: p. 85, Pl. 41.e; GODET, 2006: p. 47, Fig. B.9/E), both in "Urgonien jaune" and "Pierre jaune" units. Apart from the highly speculative

assumptions of BLANC-ALÉTRU (1995: p. 107. See the excerpt \*), these features were interpreted as evidence for subaerial exposure and as a reliable criterion to identify sequence boundaries above these intervals.

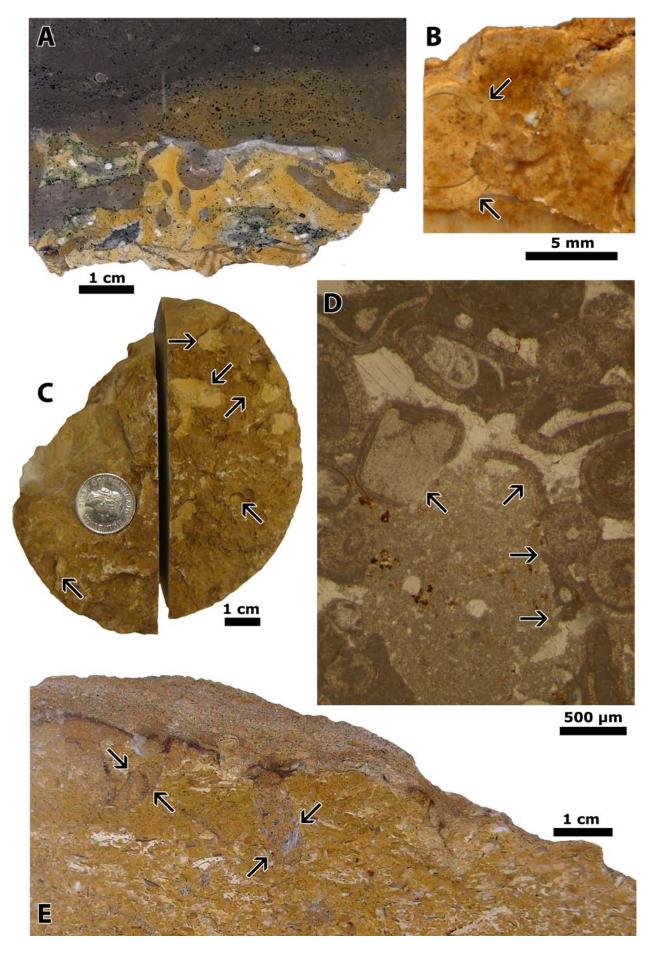
### III - Material and methods

With a sample spacing of one per metre over the 37-388 metre interval, some 350 standard petrographic thin-sections cover the whole cored section. Nearly 70 thin-sections can be referred to oolites (Fig. 2, in red), dominantly oolitic grainstones, with some oolitic wackestones and mixed bioclastic-oolitic facies; ooid cortices are partly leached in more than half of them (Fig. 2, in blue). In the upper "Pierre jaune" *auct.*, the ratio is even higher; for instance, dissolution affected the ooids over more than 15 successive thin-sections, *i.e.*, over a continuous oolitic sequence more than 14 metres thick.

Uncovered polished thin-sections from the samples were examined under a cold-cathode luminescence instrument from OPEA (Laboratoire d'Optique Électronique Appliquée, Vincennes, France) mounted on a petrographic microscope (Olympus, BX-50). The electron beam is obtained from a metal blade to reach a negative electrical potential relative to the support of the sample. A cold cathode source electron gun was chosen for its ability to produce a stable electron beam (intensity-current fluctuations < 1%). Observations were carried out at an accelerating voltage of 17-20 keV and an operating current of 250-400 mA. Images were collected with a QUICAM Imaging Fast1394 digital camera in time-integration mode using the Archimed Pro Microvision. Good quality photomicrographs were obtained by the stacking of single images.

Seven oolitic samples were selected from the upper "Pierre jaune" (152, 154, 160.25, 166, 167, 168, and 170 m) for cathodoluminescence imagery.

<sup>&</sup>quot;La présence dans une même lame d'ooïdes altérés et dissouts orientés aléatoirement, associés à d'autres ooïdes dans le cortex n'est pas dissout, indique que ces ooïdes à cortex dissout ne se sont pas formées in situ, mais ont été transportées. Ceci implique aussi que la dissolution du cortex, puis le colmatage par de la calcite de la cavité ainsi créée correspondent à deux stades successifs précoces, donc synsédimentaires." [The occurrence in the same thin section of altered and dissolved ooids, randomly oriented, and of ooids with undissolved cortices suggests that the first group ooids were not produced in situ, but were transported. It also implies that the dissolution of the cortices followed by the calcitic plugging of the resulting cavity corresponds to two successive early (i.e., synsedimentary) stages.]



#### IV - Discussion

## A) Transmitted light petrography

In the grainy oolitic facies the calcitic cement in place of the former primary porosity is typically drusy, with crystals increasing in sizes toward the centre of the inter- or intragranular space. Former aragonitic skeletal grains are represented by micrite envelopes filled by the same drusy cement (Fig. 4.I). Some echinoderm fragments develop the classic syntaxial cement, locally in the form of large poikilotopic crystals; others have a microbial coat and did not develop any overgrowth. In places a thin fringe of fibrous, probably high-Mg calcite cement (Fig. 6.A, 6.C) preceeds the drusy, probably low-Mg calcite cement. Finally, the cement filling the remaining secondary porosity, partly dissolved ooid cortices or open fractures (thin breaks as in Fig. 6.C or larger fractures Figs. 4.H, 5.A-B), is also drusy but it differs from the previous type in that it looks more transluscent (Figs. 4, 6.A, 6.C); in addition, it is more blocky, possibly because there were fewer active nucleation sites to promote crystal precipitation on the walls of the moldic cavity. There are several families of fractures (Fig. 5.A); some fractures (Fig. 5.B) might be cemented by large (?) dolomite crystals [note: this identification is uncertain since thin-sections were not stained].

Since ooid cortices show various stages of dissolution, earlier studies (BLANC-ALÉTRU, 1995; CARRIO-SCHAFFHAUSER, 2005; GODET *et al.*, 2005; GODET, 2006) concluded that these features are related to an early diagenetic event associated with subaerial exposure at a sequence boundary. However, the difference observed in the transparency and the blockiness of the two types of drusy cement suggests it might not be as simple as it first seemed.

Since these ooid cortices mostly consist of an outer drusy calcitic part (cement) and an inner fibro-radial part (almost unaltered), one might have also assumed that these ooids were "two-phase" or "bimineralic" ooids with an outer primarily aragonite cortical part and an inner primarily calcite cortical part. However, some radial-fibrous cortical layers are interrupted obliquely by the dissolution front (Figs. 4.A, 4.F, 6.A), a fact that contradicts the previous interpretation.

In addition, many ooid nuclei remained in the same position that they occupied before dissolution take place. These 'suspended' nuclei (Fig. 4.A, 4.E, 4.G) appear to float in a "blocky" drusy sparite, rather than falling to the bottom of the cortical moldic cavity. The leaching was probably incomplete and with something, either organic (the most likely) or mineral or a combination of the two, maintaining the nuclei in its original position before its peripheral cementation.

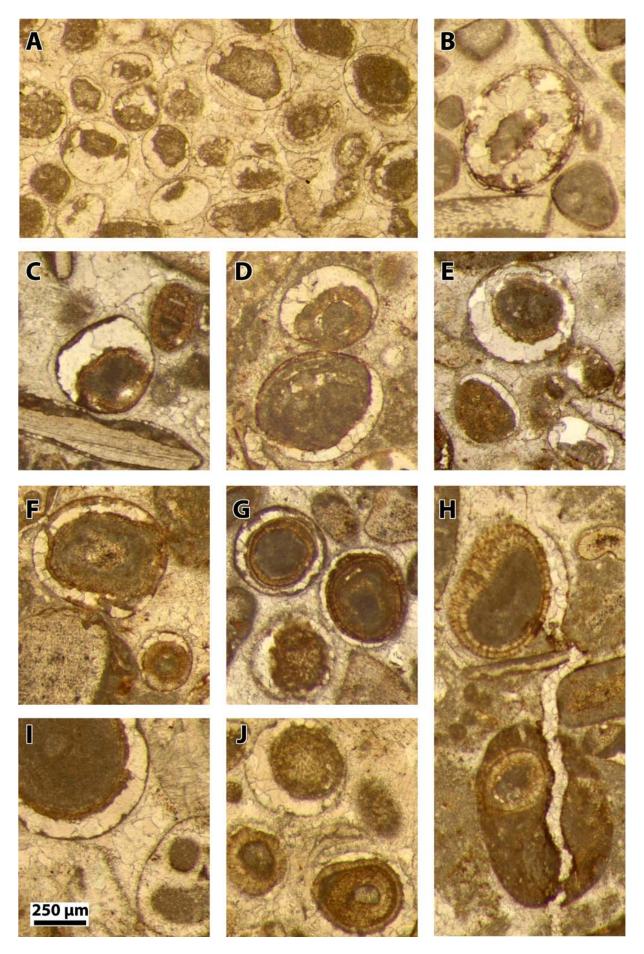
In conclusion, since the well-preserved radial-fibrous fabric is characteristic of primarily calcite ooids, and because within the same cortex some layers are both partly leached and partly preserved, it can be assumed that these ooids were primarily high-Mg calcite, not two-phase (aragonite and calcite).

#### B) Cathodoluminescence petrography

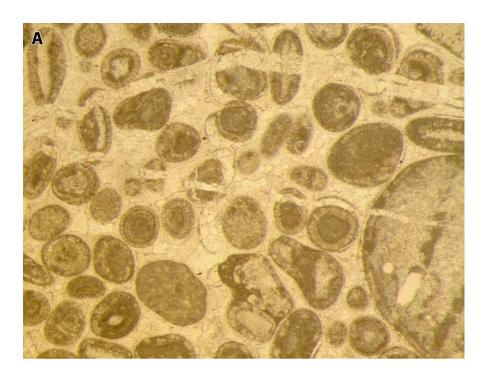
Cathodoluminescence is widely used in all aspects of petrographic studies (PAGEL et al., 2000; Boggs & KRINSLEY, 2010, inter alia). Cathodoluminescence imaging is particularly used to identify porosity loss or to distinguish different cement generations (see case studies in: Granier, 1994; Granier & Staffelbach, 2009, inter alia).

The fibrous cement fringe, inferred to have been the result of early marine cementation, is non-luminescent calcite, probably high-Mg calcite. It is also the case with the proximal (early) phases of crystal-growth in the syntaxial cement on the echinoderm grains and in the dull crystals of the intergranular drusy cement. There a black-dark brown zone is commonly followed by a reddish brown-orange alternation and then by a final yellow stage (Fig. 6.F). These zones are also present in the former aragonitic skeletal grains, but the cement filling partly dissolved ooid cortices luminesces in discrete orange-chocolate brown tones (Fig. 6.B, 6.C, 6.E, 6.G), contrasting with the previous shades of colour [Remark: the tones might vary from one picture to another, depending on the photo session or later digital alteration]. These tones are not part of the sequence: they clearly post-date it. In conclusion, the dissolution of the ooid cortices preceeded their future cementation, but it followed an earlier burial cementation stage. These observations support the earlier conclusion that the dissolution of the ooid cortices and their cementation are late diagenetic events, not early ones.

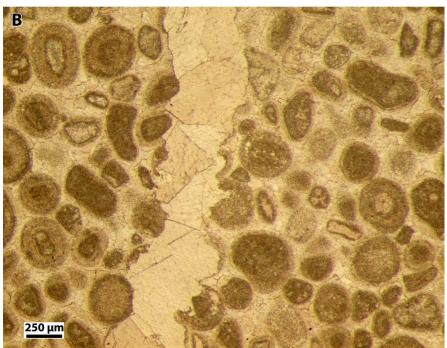
▼ Figure 3: A: 172.45 m (scale bar: 1 cm) slab with the bored hardground at the lower-upper "Pierre jaune" boundary; B: 92.42 m (scale bar: 5 mm) slab with the bored hardground at the "Urgonien jaune" - "Urgonien blanc" boundary; C: 92.42 m (scale bar: 1 cm) transverse view of a core documenting the bored hardground at the "Urgonien jaune" - "Urgonien blanc" boundary; D: sample 122 m (scale bar: 500 μm) thin-section documenting a boring in a small oolitic lithoclast in the "Urgonien jaune"; E: sample 149.30 m (scale bar: 1 cm) slab with the bored hardground at the "Pierre jaune" - "Urgonien jaune" boundary.



▼ Figure 4: A-B: "Urgonien jaune"; C-J: "Pierre jaune de Neuchâtel". A: 94 m, partly leached cortices; B: 112 m, partly leached ooid; C: 166 m, partly leached ooid; D-F: 167 m, partly leached cortices with a 'suspended' nucleus in E; G-H: 168 m, G: partly leached cortices; H: fracture with rather transluscent cement; I-J: 170 m, I: the cement in the former intergranular or biomouldic porosity is less translucent than that in the former oomouldic porosity; J: partly leached cortices [All photomicrographs same scale bar 250 µm].



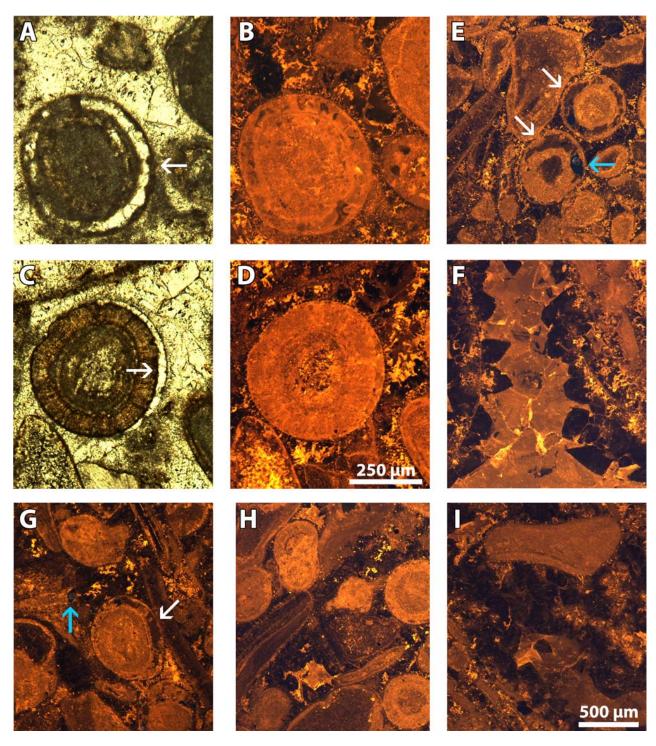
■ Figure 5: A-B: "Urgonien jaune". A: 93 m, two families of fracture, the subhorizontal ones are cutting the vertical one; B: 109 m, a fracture cemented by large (?) dolomite crystals [All photomicrographs same scale bar 250 µm].



How could dissolution have occurred? The most probable scenario is to consider that acidic waters seeped into the cemented oolitic rocks, probably through a fracture network, possibly tectonic, or karstic, during the Alpine orogeny. Later, the brines circulating in the open fractures favoured their subsequent cementation and that of the dissolved ooid cortices by

a "blocky" drusy sparite or (?) dolosparite.

Why were only the ooid cortices leached? Leaching did not affect the micritic mud, other calcareous grains, micrite envelopes, the ooid nuclei nor the sparitic cement; only ooid cortices are partly or fully dissolved. The dual nature, mineral and organic, of the ooid cortices



**Figure 6:** A-I: "Pierre jaune de Neuchâtel". A-D and F: 168 m. A-B: partial leaching of the outer cortical layers (A: conventional transmitted light; B: cathodoluminescence); C-D: break/tiny fracture at the outer surface of an ooid, between the ooid cortex and the early cement. Such a break can be compared with those observed along the vertical fracture on Fig. 5.A (C: conventional transmitted light; D: cathodoluminescence); E and G: 167m. E: white arrows for the chocolate brown cement filling the partly dissolved cortex and blue arrow for an hole -with air bubble- in the thin-section preparation (cathodoluminescence). F: cementation of a large (?) bioclast porosity by the successive early black-dark brown, median reddish brown-orange, and late yellow stages (cathodoluminescence). G: white arrow for the chocolate brown cement filling the partly dissolved cortex and blue arrow for a hole -with air bubble- in the thin-section preparation (cathodoluminescence). H: 166 m, cementation of intergranular porosity by early black-dark brown and median reddish brown-orange stages (cathodoluminescence). I: 170 m, cementation of intergranular porosity mostly by the early black-dark brown stage (cathodoluminescence) [A-D scale bar 250 μm; E-I scale bar 500 μm].

(see Dangeard, 1936; Bathurst, 1967, 1968; TRICHET, 1968; GRANIER, 1995, 2014, inter alia, and for examples of experimental ooids see LALOU, 1957a, 1957b; BREHM et al., 2004, inter alia) is probably a key to understand this selective dissolution. A late oxidation of the organic matter within the ooid cortices is possibly responsible for a microporosity, which could have favoured the dissolution of the tiny radial-fibrous crystals by an increase of their contact surface with acidic waters. It is noteworthy in this context that the dissolution is always centripetal, the innermost cortical layers remain unaltered in some cases. Several hypotheses can be considered, but no firm conclusions can be made. For example: 1) the ratio of mineral to organic material or 2) the degree of oxidation of the organic matter might have varied from the inner to the outer cortical layers, or 3) the centripetal oxidation process was interrupted due to the lack of sufficient time.

#### V - Conclusions

In both of the Hauterivian oolitic units studied, many ooid cortices were partly leached and the ooid nuclei commonly appear to float in the middle of the resulting mouldic cavities. However, as highlighted by Granier (2014): "the statement that aragonitic ooids are commonly dissolved does not imply the converse, i.e., that dissolved oolds were originally aragonitic". Actually the remaining radial-fibrous fabric of the ooid cortices suggest that these calcareous ooids were originally calcitic, not aragonitic, not "bimineralic", nor "two-phase". The organic material present in the ooid cortices is probably a key factor to explain features such as the incomplete cortical leaching and 'suspended' nuclei. Since the dissolution and the subsequent "blocky" drusy cementation postdate the intergranular drusy cementation (there are two discrete drusy phases), both phenomena are considered to be late diagenetic events. Dissolution is probably related to tectonics and/or karstification that favoured the seepage of acidic waters. As documented herein and contrary to previous assertions, ooid leaching is not necessarily an early diagenetic feature affecting aragonitic or "two-phase" ooids in relation to subaerial exposure.

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