Abstract: Calcitic ooids and bothryoids from the Yacoraite Formation in the provinces of Jujuy and Salta (Argentina) display radial fabrics pointing to their primarily high-Mg calcite (HMC) nature. The present publication documents some specimens that are partly or fully leached or recrystallized, which raises fundamental questions about the validity of some concepts, such as the very existence of the so-called "two-phase"/"bimineralic" ooids. It is assumed here that the organic content in the oolitic cortices (and, subsequently, its degree of oxidation) is the key to explaining some differential diagenetic alterations.

Key-words:
• high-Mg calcite;
• aragonite precursor;
• bimineralic ooids;
• radial fabrics;
• leaching;
• recrystallization;
• Argentina

Citation: GRANIER B.R.C. & LAPOINTE Ph. (2022).- The KALKOWSKY Project - Chapter III. Significance of primary radial fabrics associated with ancient partly leached or recrystallized calcareous ooids. Carnets Geol., Madrid, vol. 22, no. 5, p. 149-160.

Résumé : Le Projet KALKOWSKY - Chapitre III. Importance des textures radiaires primaires associées aux anciens ooides calcaires partiellement dissous ou recristallisés.- Les ooides et les bothryoids calcitiques de la Formation Yacoraite dans les provinces de Jujuy et de Salta (Argentine) présentent des textures radiaires attestant qu’ils sont principalement constitués de calcite fortement magnésienne (HMC). Cet article rapporte l’existence de quelques spécimens partiellement ou totalement dissous ou recristallisés, ce qui soulève des questions fondamentales sur la validité de certains concepts tels, par exemple, que celui suggérant l’existence d’ooïdes pouvant comporter deux phases minérales distinctes. Nous suggérons ici que le contenu organique du cortex oolithique (et, par la suite, son degré d’oxydation) permettrait d’expliquer certains phénomènes d’altérations diagenétiques différenciées.

Mots-clés :
• calcite fortement magnésienne ;
• précurseur aragonitique ;
• ooides biminéraux ;
• texture radiaire ;
• lessivage ;
• recristallisation ;
• Argentine
1. Introduction

Although in the literature some earlier authors theorized that the radial oolitic structure is a secondary acquirement, i.e., a result of diagenesis (e.g., Cayeux, 1931; Shearman et al., 1970), there is now a common agreement that the radial structure of either high-Mg calcite (HMC) or aragonite ooids is primary (e.g., Kahle, 1974; Sandberg, 1975; Tucker, 1984, amongst others).

Following the preceding contributions (Granier & Lapointe, 2021, 2022), this new chapter of the Kalkowsky Project chiefly concerns calcareous coated grains, more specifically calcite radial ooids, the cortices of which are made of HMC fibers perpendicularly orientated, and their diagenesis. Its purpose is to report and elaborate on the distinctive habits of CaCO₃ crystals can aid in the petrographical identification of their polymorphs. For instance, the fibrous crystal habit corresponds to HMC (Folk, 1974, Fig. 4 left), whereas the blocky crystal habit is characteristic of LMC (Folk, 1974, Fig. 4 right). In previous papers (Granier & Lapointe, 2021, 2022), the term "fibrite" was used to refer to the yellowish "fibrous calcite" that commonly forms the cortical layers of ooids - and that cannot be confused with "radialxial fibrous calcite" - . On the basis of its crystal habit, it was then assumed that this cortical fibrite consists of HMC (e.g., Folk, 1974). The yellow tinge of radial HMC ooids for instance matches the yellow tinge of HMC echinoderm bioclasts (e.g., Granier, 2019, 2020); thus the yellow tinge is a relic of a primary organic presence. Besides calcite (both low- and high-Mg calcites), aragonite is the other common polymorph with needle-like crystals; these needles are much thinner than fibers per definition, and commonly arranged in bundles. Spherulites and some ooids have radial fabrics that are directly related to the arrangement of calcite fibers or aragonite needles, the long axes of which are orientated perpendicular to the oolitic cortical layers, whereas the aragonite needles in Bahamian ooids (and in those from the Persian Gulf, as in Fig. 1) have their long axes tangentially orientated within the oolitic cortical layers.

In most calcitic ooids with radial-concentric fabrics, thin micrite layers delimit thicker fibrite growth bands. The thicknesses of these bands are responsible for the more or less visible radial pattern of the oolitic fabrics whereas the density of micrite layers (hence the number of fibrite interlayers) is responsible for their more or less visible concentric pattern. Because all transitional fabrics from a radial extreme to a concentric extreme may exist, making out their formal division into sub-categories is rather artificial. For instance, Granier (1994a, 1994b, 1994c, 1995a, 1996) describes an overall gradational sequence from calcitic "radial ooids" at the bottom of a Lower Callovian oolite in the Villeperdue oilfield (Paris Basin, France) passing to (radial-) "concentric ooids" in the median part and then to (concentric) "micritic ooids" at the top of the logged sections. Fortunately, in this case study, the occurrence of two short hiatuses in sedimentation permitted that author to sort these ooids into three subcategories, namely radial, concentric and micritic. For instance, in the case of the VPI-01 well (Infoterre), located 1.2 km S of Le Gault-Saigny (Marne), 100 km E of Paris, the radial/concentric and the concentric/micritic boundaries are respectively located at circa 1816 m and 1827 m core depths (Fig. 2). Note that the micritic ooids are not micritized ooids, but ooids with numerous micrite layers and very thin fibrite growth bands.

2. Generalities on the mineralogies

As stated in the essentials of carbonate petrography summarized in Folk's (1974) seminal paper the distinctive habits of CaCO₃ crystals can aid in the petrographical identification of their polymorphs. For instance, the fibrous crystal habit corresponds to HMC (Folk, 1974, Fig. 4 left), whereas the blocky crystal habit is characteristic of LMC (Folk, 1974, Fig. 4 right). In previous papers (Granier & Lapointe, 2021, 2022), the term "fibrite" was used to refer to the yellowish "fibrous calcite" that commonly forms the cortical layers of ooids - and that cannot be confused with "radialxial fibrous calcite" - . On the basis of its crystal habit, it was then assumed that this cortical fibrite consists of HMC (e.g., Folk, 1974). The yellow tinge of radial HMC ooids for instance matches the yellow tinge of HMC echinoderm bioclasts (e.g., Granier, 2019, 2020); thus the yellow tinge is a relic of a primary organic presence. Besides calcite (both low- and high-Mg calcites), aragonite is the other common polymorph with needle-like crystals; these needles are much thinner than fibers per definition, and commonly arranged in bundles. Spherulites and some ooids have radial fabrics that are directly related to the

3. Material and general setting

Most ooids studied below display radial-concentric fabrics similar to the Paris Basin ooids. However, they are found associated with partly and fully replaced ooids, partly leached ooids, or both. Some calcite ooids (Fig. 2) from the Paris Basin (Villeperdue, at 48°48'19.0"N 3°35'42.0"E) and some aragonite ooids (Fig. 1) from the Abu Dhabi offshore (Abu Al Bukhoosh, circa 25°29'37.3"N 53°07'38.6"E) are also illustrated herein but only for comparison purpose.
Figure 1: Aragonite ooids from ABK wells (Abu Al Bukhoosh oil field, Abu Dhabi offshore), Pleistocene: A-D) one cortical layer was oxidized and leached, ABK PP53, 25.25 m; E-F) two discrete cortical layers were oxidized and leached, ABK S1, 25 m; G-H) ABK S1, 24.5 m. In all cases, an intergranular “dog-tooth” calcite cementation precedes the aragonite leaching that affected a few cortical layers only. B, D, F) Crossed polarizers. Scale bars 100 µm (photos A-B) and 50 µm (photos C-H).
**Figure 2:** Calcite ooids from the VP101 well (Villeperdue oil field, France), lower Callovian: "radial" ooids (A-B); "concentric" ooids (C-D); "micritic" ooids (E-F). A) 1828 m core depth, B) hiatus ooid on the right, 1827.75 m CD, C) 1836 m CD, D) 1816.75 m CD, E) 1811.10 m CD, F) 1806.75 m CD. Scale bar 50 µm (all photos).

**Figure 3:** A) Location map of the provinces of Jujuy (red) and Salta (blue), N Argentina; B) location map of the studied sections in N Argentina; C) location of sampling 339 (Jujuy); D) location of samplings 269-270 (Salta).
The Argentinian material shown here was collected by one of us (P.L.) accompanied by three IFP colleagues (namely Bernard Colletta, Jean Létozé, and Roland Vially) at two discrete localities (Fig. 3):

1) on October 6, 1988. The first section measured (Figs. 4 - 5) crops out some 60 km south of Salta, more precisely at 25°17’04.4”S 65°24’-56.1”W (Province of Salta, Argentina), on the northern side (left hand side) of the road 47 from Coronel Moldes to Puente Dique Cabrera Corral (Fig. 3.B, D), on a bend with a view to the "embalse" (dam) Cabrera Corral. It is located in the Metán subbasin of the Salta Basin. Although in the initial (unpublished) report it was ascribed to the Maiz Gordo Formation (MORENO, 1970), Tha- netian-Ypresian in age [Late Paleocene - Early Eocene in age (e.g., DEL PAPA, 1999)], this section, appears in a recent contribution of FREIRE (2012) as "Afflamento Viñuales" of the "Seqüência Bacluena IV" (op.cit., Figs. 5.1, 5.10, 8.7) of the Yacoraite Formation and is currently ascribed a Danian age. Four petrographic thin sections were prepared from two pieces of rock labelled ARA 269 and ARA 270. They were picked at the top of the logged section: The two first thin sections (ARA 269 and ARA 270) are probably lost; the two second thin sections (AG 269 and AG 270) were prepared from offcuts of the first two;

2) on October 13, 1988. The second section was measured (Fig. 6) in Arroyo El Fuerte. It crops out 6 km south of El Fuerte, some 45 km SSW of Palma Sola and some 85 km east of San Salvador de Jujuy (Fig. 3.B-C), circa 24°17’-55.0”S 64°27’42.7”W (Province of Jujuy, Argentina). It is located in the Lomas de Olmedo subbasin of the Salta Basin. It spans the boundary of the Lecho and Yacoraite formations and comprises strata that are ascribed Campanian-Maastrich- tian ages. Two petrographic thin sections were prepared from one piece of rock labelled ARA 339. It was picked near the bottom of the logged section: The first thin section (ARA 339) is probably lost, the second thin section (AG 339) was prepared from an offcut of the first one.

4. Description of the thin sections prepared from samples ARA 269-270 (Salta) and ARA 339 (Jujuy)

1) The Salta microfacies (ARA 269-270): The microfacies of thin section AG 269 corresponds to a floatstone of bothryoids (Fig. 7.N) and large cerebroid ooids (Fig. 7.F) with a wackestone silty matrix. In addition to the siliciclastic silt, the matrix yields smaller ooids and fish teeth. Ostracod shells are also present, commonly as nuclei of coated grains. One third of the thin section AG 270 exhibits the same facies; its remaining two thirds displays a mudstone texture.

2) The Jujuy microfacies (ARA 339): The microfacies of thin section AG 339 corresponds to an oolitic grainstone. Besides the ooids, allochthones comprise few micritic extraclasts. Ostracod shells are common, mostly as oolitic nuclei.

5. Interpretation of some oolitic features from samples ARA 269-270 (Salta) and ARA 339 (Jujuy)

The mineralogy of the ooids and bothryoids of ARA 269-270 (Salta) and that of the inner cortices of the ooids of ARA 339 (Jujuy) are largely, if not exclusively, HMC. Locally, the two formers show evidence of recrystallisation whereas the latter was partly affected by recrystallisation but also by leaching and cementing.

1) Salta ooids and bothryoids (ARA 269-270, Fig. 8): In thin section (hence in two-dimensional view), some oolitic cortices yield scattered or amalgamated (i.e., forming an idiotopic mosaic) polygonal sections of calcite crystals up to 50 µm in width. At first sight they could be confused with transverse sections of the "clubs" described by HALLEY (1977, Fig. 3.c-d) from the Great Salt Lake aragonite ooids, but whatever the ooid section is, tangential or deep (hence in reconstructed three-dimensional view), the crystal shape remains blocky, not pillaroid. These crystals still retain a yellowish color related to the original organic content. They correspond to the recrystallisation of fibrous HMC into blocky LMC.

2) Jujuy ooids (ARA 339, Fig. 9): Most calcite ooids from thin sections ARA 339 and AG 339 comprise two parts: 1) an outer part, i.e., the outer cortex, and 2) an inner part consisting of the inner cortex and the nucleus, e.g., quartz grain. When preparing the thin sections the inner parts of some ooids were ripped off but when they are preserved they commonly consist of an ooid with a radial-concentric fabric (Fig. 9). Again the inner cortex is probably made of HMC coalescent fibers, the brownish color of which contrasts with the overall yellowish color of the outer cortex. The outer cortex displays a concentric fabric with relics of growth bands and an alternation of yellowish layers and hyaline layers.
Figure 4: Cabra Corral outcrop. A) View from the South; B) view from the East; C) structural surface with the uppermost stromatolites; D) close-up on the uppermost stromatolites.

Figure 5: Cabra Corral section. A) alternation of green claystones and marlstones; B) schematic drawing of the Salta section (Cabra Corral) with location of samples 269 and 270; C) uppermost stromatolites; D) alternation of lime mudstones and claystones (more or less silty); E) lowermost stromatolites.
Figure 6: Schematic drawing of the Jujuy section (El Fuerte) with location of sample 339.

Tangential sections, which per definition do not reach the ooid inner part, are the most suitable to document the morphology of the LMC crystals of the outer cortex. Yellowish crystals, blocky in shape and almost equidimensional, form an hypidiotopic mosaic as a result of recrystallisation of some outer cortical layers. When the recrystallized layers are relatively thick, their fabric may be similar to the "brick-like texture" of some Italian Triassic pisoliths described by Assereto and Folk (1976). On the other hand, hyaline crystals correspond to the drusy cementation of voids left by leaching after some other outer cortical layers. The typical arrangement of the drusy cement with crystals sizes increasing centripetally is better seen when the cavities are relatively large. Some crystals are both colored and hyaline (as is also the case with an echinoderm remain and its syntaxial cement, e.g., Granier, 2020, Fig. 1A-B) at the transition from replaced areas to cemented areas. That suggests that part of the cement crystals represents syntaxial overgrowths of replacement crystals.

6. Extended discussion on the Jujuy ooids (ARA 339)

According to generally accepted -but commonly erroneous- views, it is claimed that most recrystallized or leached ooids suggest an aragonite precursor in their oolitic cortices [*] whereas those with partly replaced or leached cortices are interpreted as "two-phase" or "bimineralic" (Buczynski & Wilkinson, 1982; Tucker, 1984; Chow & James, 1987; Heydari & Moore, 1994; Algeo & Watson, 1995). Probably because common bioclasts such as originally HMC echinoid remains do not show obvious signs of recrystallization or leaching, the earlier authors did not really imagine the option that fully or partly recrystallized or leached ooids could have originally been "monomineralic", i.e., made mostly of HMC. This was appreciated by Granier (2014) who

Hollis C., Lawrence D.A., Deville de Perière M. & Al Darmaki F. (2017).- Controls on porosity preservation within a Jurassic oolitic reservoir complex, UAE.- Marine and Petroleum Geology, vol. 88, p. 888-906. (see Fig. 6)
Figure 7: Various morphologies of coated grains:
A) regular ooid; B) superficial ooid; C) hiatus ooid, regenerated; D) hemiooid or broken ooid sensu stricto; E) broken ooid sensu lato, broken but regenerated; F) cerebroid or pitted ooid; G) oolitic lithoclast with borings; H) aggregate with two ooids; I) superficial biooid or superficial complex ooid; J) biooid or complex ooid; K) aggregate or grapestone (initial amalgamation stage); L) lump (advanced amalgamation stage); M) superficial bothryoid; N) bothryoid.
argued that "the statement that aragonitic ooids are commonly dissolved does not imply the converse, i.e., that dissolved ooids were originally aragonitic". Subsequently, finds questioning the earlier views showed up in discrete case studies from the Middle Jurassic of France (GRANIER, 1995b, 2014), the Lower Cretaceous of Switzerland (GRANIER et al., 2014, 2016), and the Middle Cretaceous of Angola (GRANIER, 2019). Likewise, partly recrystallized Salta ooids and bothryoids (ARA 269-270) represent one more case study to add to the reference list because they document the replacement of HMC (not aragonite) by LMC. The Jujuy ooids (ARA 339, Fig. 9), as the Hauterivian ooids from Switzerland (GRANIER et al., 2014, 2016) before, represent a more tricky case: 1) the inner cortex is made of brownish HMC fibers with a radial-concentric habit; 2) the outer cortex is made of LMC crystals, either yellowish blocky (replacement) or hyaline drusy (cement). Based on existing literature (BUCKYNSKI & WILKINSON, 1982; TUCKER, 1984; CHOW & JAMES, 1987; HEYDARI & MOORE, 1994; ALGEO & WATSON, 1995), these Jujuy ooids could have been interpreted as "two-phase" or "bimineralic", i.e., HMC for their inner cortices and aragonite for their outer cortices, but a more credible option is outlined below.

Long before the first author (GRANIER, 1995b, 2014; GRANIER et al., 2014, 2016) several authors (e.g., DANGEARD, 1936; NEWELL et al., 1960; FREEMAN, 1962; TRICHET, 1968; SHEARMAN et al., 1970; KAHELE, 1974; SANDBERG, 1975; HALLEY, 1977) agreed upon the dual nature, mineral and organic, of oolitic cortices. However, a few among them stressed a possible significant impact of the organic content (its presence or its removal through oxidation) during diagenetic processes (e.g., SHEARMAN et al., 1970; SANDBERG, 1975; GRANIER, 1995b, 2014; GRANIER et al., 2014, 2016).
In the case of Pleistocene ooids from Abu Dhabi, some cortical layers of the aragonite ooids could be missing (Fig. 1). It is suggested that, in these specific layers, the oxidation of the organic matter in the meteoric vadose zone facilitated the leaching of aragonite by acidic fresh-water. This model for Pleistocene aragonite ooids can easily be transposed to ancient HMC ooids. With this picture in mind, the "two-phase" or "bimineralic" model stumbles.

According to Tucker (1984), "Two phase ooids could either reflect" 1) "the reworking of ooids from one area into another where a different mineral was being precipitated, or" 2) "some change in the physico-chemical conditions at the site of ooid formation, causing a change in the carbonate mineral being precipitated". Both hypotheses, to be valid, need to be two-way processes. However, to our knowledge, that is never the case. When an ooid has both an inner cortex and an outer cortex the layers of the former remain unaltered whereas there is no record of ooids with unaltered outer cortical layers and recrystallized or leached and cemented inner cortical layers. The alternative hypothesis presented in the case of the Haurterivian ooids from Switzerland (Granier et al., 2014, 2016) suggests that the key features explaining the centripetal diagenetic processes are related to the organic content in their oolitic cortices, e.g., "the ratio of mineral to organic material" and variations of "the degree of oxidation of the organic matter" within discrete cortical layers, as well as the more or less advanced "centripetal oxidation process". The latter authors (Granier et al., 2014, 2016) further concluded that the Swiss ooids were originally monomineral, i.e., made almost exclusively of HMC. This last hypothesis is the only one tenable that explains the fabrics of the Jujuy ooids (ARA 339). *Ipso facto* it is also a valid hypothesis for explaining many earlier so-called "two-phase" or "bimineralic" ooids (actually probably mostly monomineralic ooids with HMC cortices).
7. Conclusions

On the basis of the present study and reinterprated observations from our predecessors, it is proposed that:

1) ancient HMC ooids and aragonite ooids could never occur in the same sample, i.e., they probably never occurred at the same time in a same location, and 

2) the association of radial fabrics with partly or fully leached or recrystallized calcite ooids points to original cortices being composed mostly of HMC, and neither of aragonite nor with a "two-phase," "bimineralic" nature.

The logic behind this proposed hypothesis is that it is unlikely geochemical settings favoring either HMC ooids and/or aragonite ooids occur adjacent to one another, and to date no two such settings have ever been seen.

Acknowledgements

This paper is dedicated to our former colleague, the late Edmond Ousset (1954-2021). Amongst other responsibilities during his full career with Total, he was Chief Geologist in "Filiale France" at Paris La Défense from 1988 to 1991 and Exploration Manager in Total Austral at Buenos Aires from 1995 to 1998. The Argentinian material studied here was collected by the second author (R.L.) during a joint mission of Total - Compagnie Française des Pétrôles, and IFP - Institut Français du Pétrole from October 5 to November 3, 1988. He acknowledges the support of his IFP colleagues, Bernard Colletta, Jean Letouzey, and Roland Vialy, for fieldwork. The first author (B.R.C.G.) would like to thank Phil Salvador for his appreciated help with the original (English) text and to Christopher G. St. C. Kendall for a stimulating discussion on radial HMC ooids.

Bibliographic references


the Great Salt Lake and the geological re-
relationships in a stromatolite from the Maiz no. 3, p. 111-117.

dr. vol. 14, no. 21, p. 461-469.

New stratigraphic and genetic model for the dolomitic Cretaceous Pin-
dara reservoirs in Angola. Part II - Compelling arguments against early dolomitization and early leaching.- Carnets Geol., Madrid, vol. 19, no. 4, p. 47-70.

The biosignature of sparite permits the distinction between gravitational cement and endostromatolites.- Carnets Geol., Madrid, vol. 20, no. 20, p. 407-419.


Comments on "Estimating the impact of early diagenesis on isotope records in shallow-marine carbonates: A case study from the Urgonian platform in western Swiss Jura" by A. GODET et al. [Palaeogeography Palaeocli-

The KALKOW-
SKY Project - Chapter I. Ooid - stromatoid relationship in a stromatolite from the Maiz Gordo Fm (Argentina).- Carnets Geol., Madrid, vol. 21, no. 9, p. 193-201.

The KALKOW-

Quick look cathodoluminescence analyses and their impact on the interpretation of carbonate reservoirs. Case study of mid-Jurassic oolitic re-

Ooid fabric and fracture in the Great Salt Lake and the geological re-

Heydari E. & Moore C.H. (1994).- Paleooceanogra-
phic and paleoclimatic controls on ooid mineralogy of the Smackover Formation, Mississippi salt basin: Implications for Late Jurassic seawater composition.- Journal of Sedimentary Research, Boulder, vol. 64, no. 1a, p. 101-114.

Infoterre.- VilleperdueIO1 - VPU 44. - Dossier du sous-sol, BSS000PRKQ, retrieved February 15, 2022, from http://ficheinfoterre.brgm.fr/InfoterreFiche/ficheBss.action?id=BSS000PRKQ

Kahle C.F. (1974).- Ooids from Great Salt Lake, Utah, as an analogue for the genesis and dia-

Loreau J.-P. (1973).- Nouvelles observations sur la genèse et la signification des oolithes. In: Sédi-

Moreno J. (1970).- Estratigrafía y paleogeografía del Cretáceo Superior en la cuenca del norte ar-
gentino, con especial mención de los Subgrupos Balbuena y Sánta Barbara.- Revista de la Asociación Geológica Argentina, Buenos Aires, vol. 25, no. 1, p. 9-44.

Newell N.D., Purdy E.G. & Imbrie J. (1960).- Bah-
amian oolitic sand.- The Journal of Geology, Chi-

Sandberg P.A. (1975).- New interpretations of Great Salt Lake ooids and of ancient non-skele-

Shearman D.J., Twyman J. & Zand Karimi M. (1970).- The genesis and diagenesis of oolites.- Proceed-


Tucker M.E. (1984).- Calcitic, aragonitic and mixed calcitic-aragonitic ooids from the mid-Protero-