

## APÊNDICE G - Trabalho sendo preparado para submissão em periódico a ser escolhido

### Sustainable Production of Xanthan Gum in Wastes of the Energy Industry

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#### Abstract

Xanthan is a *Xanthomonas* polysaccharide of great commercial interest due to its properties mainly that of forming viscous solutions at low concentrations, with uses in the food, pharmaceutical and petrochemical industries, as well as for enhanced oil recovery. The present work evaluated the use of wastes from two oil-producing wells and a mixture of raw glycerin and sucrose as a medium for xanthan gum production. Values of 8.31 and 8.95 gL<sup>-1</sup> of xanthan gum with 92 and 492 cP viscosities were obtained with produced water from the A and B wells, respectively. Statistical analysis showed that sucrose was responsible for the variation of the xanthan production. Interaction of sucrose and glycerin significantly influenced the production of xanthan. Infrared absorption spectroscopy showed that both gums have a molecular structure similar to the commercial xanthan gum. Our process has been producing a good oil grade xanthan at lower cost than traditional processes.

**Keywords:** Xanthan gum; glycerin; produced water; oil recovery

#### Introduction

Xanthan gum is a natural polysaccharide and an important industrial biopolymer, discovered in the 1950's and marketed from the 1960's (Garcia-Ochoa et

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al., 2000). Synthesized by bacteria of the phytopathogenic genus *Xanthomonas*, this polymer is used by the bacterium as a factor in protection against environmental stress, desiccation, and may contribute to virulence. For humanity, it is a product of great commercial interest, due to its ability to form viscous solutions in aqueous medium, even at low concentrations (Garcia-Ochoa et al., 2000; Souza and Vendrusculo, 1999), which results in a large number of applications in different industrial segments. In addition to being used in the food sector, it is also used in the pharmaceutical, chemical and petrochemical industries, where its properties are essential to the final applications, and are determined by its chemical composition, groupings, and molecular bonds, and its average molecular weight and distribution (Pace, 1991). In the petroleum industry, the xanthan gum has been used in operations, particularly in drilling fluid and special methods of oil recovery, due to its chemical and rheological properties. The desirable polymer properties for use in these applications are high viscosity at low concentrations, as well as high pseudo-plasticity and stable behavior of viscosity in relation to salinity, temperature and alkaline conditions, among others (Shah; Ashtaputre, 1999). Brazil follows the global trend of increased consumption of xanthan gum, even though it is totally imported, demonstrating the relevance of investing in alternative domestic production methods. Brazil has great potential for production of this polymer in industrial scale because it has basic raw materials for the production (Souza and Vendrusculo, 1999). However, in other countries the cost of the fermentation medium represents a critical factor for the commercial aspect of production of this polysaccharide (Pradella, 2006). For this reason, there is an increasing interest in alternative substrates, such as industrial wastes that are currently discarded and can represent serious environmental problems, but which can be used as an alternative for the bioproduction of polysaccharides due to lower production costs. Many factors directly influence the production and properties of xanthan gum, which have been demonstrated by various researches in the area. The use of agroindustrial effluents and wastes for production of xanthan gum has become increasingly common among researchers. The residues studied in this work come from the oil industry, and from the biodiesel and agroindustrial sector. Produced water is generated during the oil production process, and its treatment has been a challenge due to its complexity and the amount of wastes generated (Santos et. al., 2005). Thus, this work aims to evaluate

the production of xanthan gum in produced water from the oil industry and raw glycerin from biodiesel production.

## Methods

### Strains

Strains of *Xanthomonas campestris* were isolated from the culture collection (CCMICS) of the Laboratório de Biotecnologia e Ecologia de Microrganismos (LABEM/UFBA), where they are stored at  $-70^{\circ}\text{C}$  in a Thermoelectron brand ultra-freezer (2006). The produced water (PW) from the oil industry was collected from two oil producing wells, identified as A and B, from the Recôncavo Basin in Bahia state, and refrigerated (at  $4^{\circ}\text{C}$ ) until the moment of use. The raw glycerin used came from the production of biodiesel by transesterification of fats and oils, kindly provided by Prof. Ednildo Andrade Torres, Coordinator of the Energy and Gas Laboratory of Escola Politécnica da Universidade Federal da Bahia.

### Inoculum for cell production

Three batches of a fresh culture grown in yeast mannitol medium (YM) agar were used as pre-inoculum to activate the bacteria in liquid YM, followed by incubation in an orbital shaker (Innova, New Brunswick) at 120 rpm for 24 hours at  $30^{\circ}\text{C} \pm 2^{\circ}\text{C}$ .

The second stage started after 24 hours, through the transfer of 1000  $\mu\text{L}$  of aseptic pre-inoculum to Erlenmeyer flasks of 300 mL, containing 50 mL of YM. The flasks were then incubated in an orbital shaker with agitation of 120 rpm, at  $30^{\circ}\text{C} \pm 2^{\circ}\text{C}$ , until they reached the optical density of 2.5 ( $\text{DO}_{560\text{nm}} = 2.5$ ), which corresponded to the late log phase of the growth curve. This absorbance is reached at 40 hours of incubation and corresponds to a cell concentration of  $10^9$  cfu.mL<sup>-1</sup>.

### Production Medium

Production media contained potassium phosphate monobasic ( $5.0 \text{ g.L}^{-1}$ ), ammonium carbonate ( $0.5 \text{ g.L}^{-1}$ ), sodium glutamate ( $0.1 \text{ g.L}^{-1}$ ) in produced water (PW) from wells A and B of the Recôncavo Basin, Bahia, Brazil. Also, a combination of different concentrations of glycerin and sucrose were added as C sources, varying according to the experimental planning presented in Table 1. Production media were pasteurized at  $65^{\circ}\text{C}$  for 30 minutes. The production medium was inoculated with 21% (v/v) of inoculum of *Xanthomonas campestris* CCMICS 507 and incubated in an

orbital Shaker at 180 rpm, 30°C ± 2°C for 72 hours. (García-Ochoa et al., 2000; Esgalhado, et al., 1995; Psomas et al., 2007).

Table 1. Variables studied and experimental planning levels.

Variables Studied	Variable Levels		
	-1	0	+1
Sucrose (%)	0	2	4
Crude Glycerin (%)	0	2	4

All trials were conducted in triplicate, where gum production was evaluated as a response variable. The effect of variables (carbon source and ratio) was tested with the aid of the software Statistica 8.0 vs.

#### Recovery of Xanthan gum

Recovery of the gum from cells of the fermented broth was done adding ethanol 96° GL (1:3, v/v). The gum was recovered after centrifugation (7000 rpm/30 minutes at 4°C). The biopolymer recovered was dried in an oven at 50°C (García-Ochoa et al., 2000; Giavasis et al., 2003; Pace, 1991). Xanthan was measured gravimetrically.

#### Apparent Viscosity

Apparent viscosities of the xanthan gum solutions at 1% (m/v) were performed in a digital brand rotorless Brookfield LVDV III + model, coupled to a bath, using the adapter for small samples, 18 spindle, which adjusts the shear rate from 0 to 264 s<sup>-1</sup> and viscosity from 1.3 to 30000 cP. The solutions were agitated and heated at 60°C until complete gum dissolution (Diaz et al., 2004; Zhang Xuewu et al., 1996). The readings were performed at intervals of 10 seconds, varying shear rate (0-264 s<sup>-1</sup>), at 25°C.

#### Molecular Structure

Xanthan gum samples produced were subjected to analysis in absorption spectroscopy in the infrared (IR) region, obtained in KBr pellets, pressed under vacuum, using a BOMEM spectrophotometer, model MB-102, in the region between 4000 and 400 cm<sup>-1</sup>. Controls were done with tablets of KBr, and KBr standard and commercial xanthan gum.

## Results and discussion

### Production Medium

Table 2 presents the matrix of experimental planning with the variation in the types and concentration of carbon sources with resulting productivity. The responses were treated as dependent variables for two way analysis of variance (ANOVA) test.

Table 2. Xanthan gum synthesized by *Xanthomonas campestris* CCMICS 507 with produced water from wells A and B, with different concentrations of carbon sources, 30° C, 180 rpm, 72 hours of fermentation.

Assays		Well A		Well B	
Sucrose (%)	Glycerin (%)	Production* (g.L <sup>-1</sup> )	Standard Deviation	Production* (g.L <sup>-1</sup> )	Standard Deviation
0	0	3,91	0,219	2,28	0,361
0	2	4,60	0,271	3,37	0,174
0	4	4,54	0,591	3,34	1,557
2	0	5,44	0,358	5,08	0,669
2	2	8,31	0,955	6,72	0,319
2	4	5,41	0,780	5,01	0,317
4	0	4,84	0,631	2,62	0,289
4	2	7,50	0,703	8,95	1,900
4	4	6,71	1,140	3,36	1,040

\*Triplicates mean

Analysis of results in Table 2, showed that the larger production came with 2% sucrose and 2% of raw glycerin using PW effluent A (8.31 g.L<sup>-1</sup>) and 4% sucrose and 2% raw glycerin using PW effluent B (8.95 g.L<sup>-1</sup>). Since the composition of this waste is quite variable, supplemental carbon source required for production of xanthan gum will change with the type of PW effluent used. It was also verified that there is production of gum without the carbon sources examined, in the PW effluent A (3.91 g.L<sup>-1</sup>) and B (2.28 g.L<sup>-1</sup>), showing that *Xanthomonas campestris* CCMICS 507 is able to metabolize carbon sources present in this type of waste, mostly hydrocarbons.

The analysis of the data showed that the interaction between the two carbon sources (raw glycerin and sucrose) was highly significant ( $p < 0.005$ ), confirming the

carbon synthesis from raw glycerin by *Xanthomonas campestris* CCMICS 507. There is no record in the literature of xanthan gum production from wastes from the oil industry, nor from the production line used in this work. Raw and pure glycerin have already been used as a substrate for the production of xanthan gum by Druzian et al. (2007), but there is no published data on the productivity of the gum.

The rotation rate used in this work, 180 rpm, was the same fixed by Fornari (2006), Luvielmo (2007), Salah et al. (2010), and Nery et al. (2008). Papagianni et al. (2001) evaluated different rotation rates on production of xanthan gum. These authors found best yield results using 600 rpm, however this could increase production costs.

Figure 1 presents the aspect of one of the samples of xanthan synthesized from the production media based on oil industry waste after 72 hours of fermentation, as obtained in this work.



Fig. 1. the aspect of xanthan gum after: (a) Precipitation with ethanol; (b) Spinning; (c) drying and grinding.

Alternative sources are being tested regularly in order to reduce costs and produce xanthan gum at competitive prices, thus justifying their use in producing xanthan for applications such as enhanced oil recovery in mature oil fields. The use of cassava serum was carried out by Brandão et al. (2010), yielding  $13.83 \text{ g.L}^{-1}$  of biopolymer at  $25^\circ\text{C}$ , 250 rpm for 120 hours with *X. campestris mangiferaeindicae* strain. According to Nery (2008), 6.7, 5.6 and  $21.91 \text{ g.L}^{-1}$  of xanthan gum were obtained from the fermentation of green coconut husk, rind of passion fruit and whey, respectively, by *X. campestris mangiferaeindicae* fermented at  $28^\circ\text{C}$ , 250 rpm for 120 hours. However, the viscosities presented by the different gums produced were no larger than 2 cP. From sugar beet molasses pre-treated and supplemented with sucrose, Kalogiannis et al. (2003) produced  $53.0 \text{ g.L}^{-1}$  of xanthan gum. The

fermentation of whey resulted in 28.0 to 13.0 g.L<sup>-1</sup> of xanthan gum, while Nitschke et al. (2001) produced 5.8 g. L<sup>-1</sup> from coffee waste. Druzian and Pagliarin (2007) produced 45 g.L<sup>-1</sup> of xanthan gum from waste from apple juice processing.

#### Apparent Viscosity

Viscosity curves as a function of shear rate for the gums are presented in Figures 2 and 3, where the pseudoplastic behavior is evident in all samples of gum produced in this work, that is, the apparent viscosity decreases with increasing shear rate. This behavior is expected in polymeric solutions of microbial polysaccharides (Kalogiannis et al. 2003; Padilha, 2003).

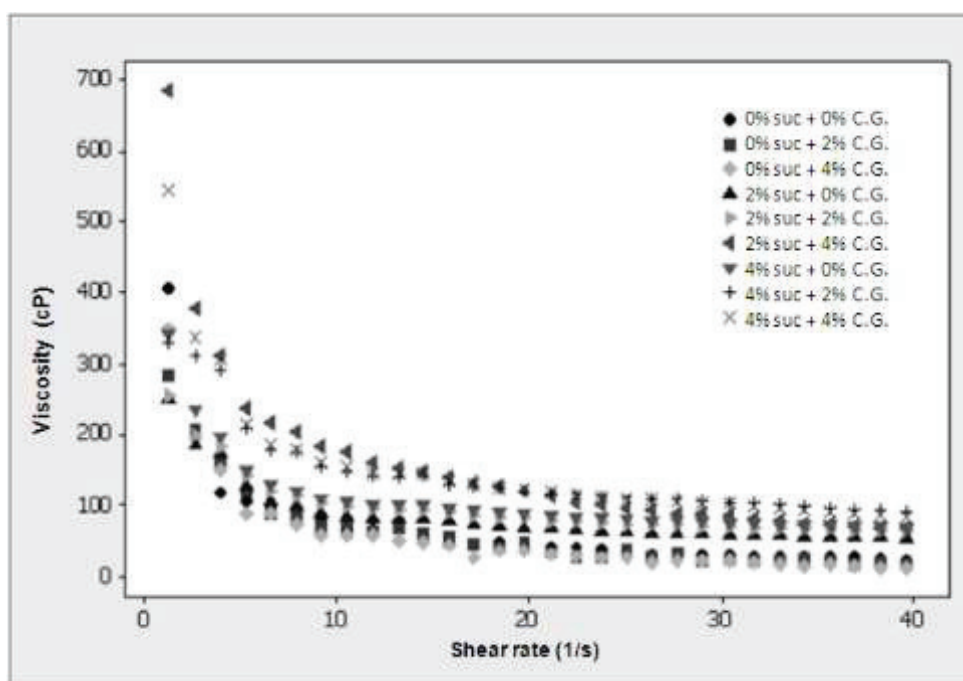


Fig. 2. Apparent viscosity of 1% aqueous solutions of gums synthesized by strains of *Xanthomonas campestris* CCMICS 507 in produced water of well A with different carbon sources. Legend: Suc – sucrose; CG - Crude Glycerin.

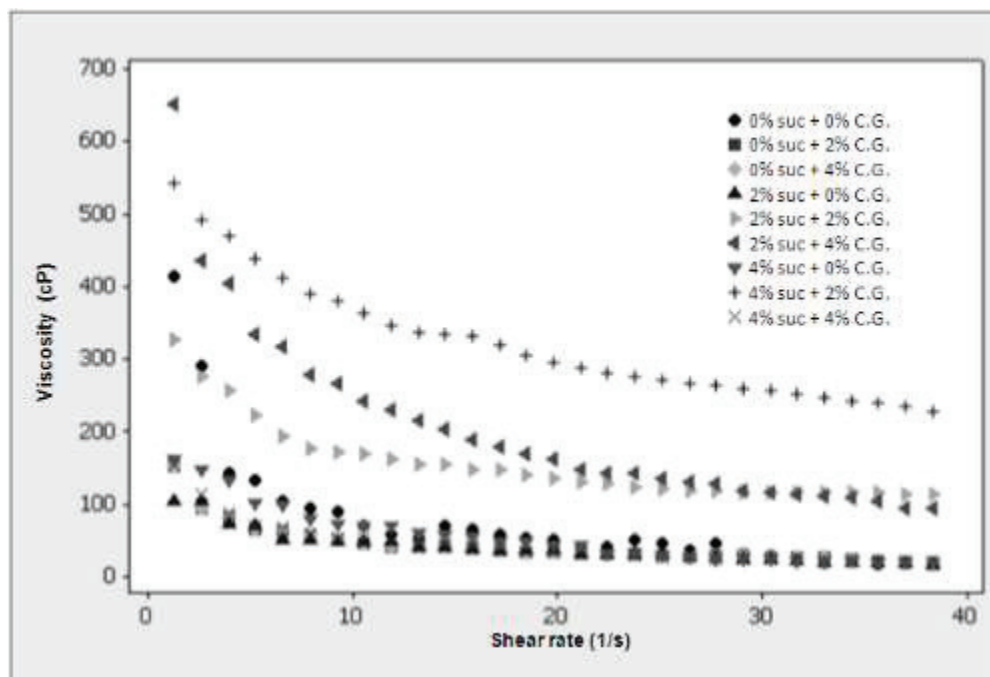


Fig. 3. Apparent viscosity of 1% aqueous solutions of gums synthesized by strains of *Xanthomonas campestris* CCMICS 507 in produced water of well B with different carbon sources. Legend: Suc – Sucrose; CG - Crude Glycerin.

Apparent viscosity was analyzed in 1% aqueous solutions of xanthan gum, at 25°C at a shear rate of 2.64 s<sup>-1</sup>, which is the smallest reading possible carried out on all samples, since the gums presented different viscosities. For the gums produced with PW of oil wells, they attained the highest viscosity, of 379 cP, with 2% sucrose and 4% glycerin. For gums produced with PW of well B, 4% sucrose and 2% glycerin, the viscosity was 434 cP. As with production, supplementation required changes according to the origin of the PW tested, because its composition is quite variable.

It is known that different operating conditions, as well as the strains used, can influence directly in the production of xanthan gum, causing different yields and viscosities. Thus, further research is needed to optimize the production of xanthan gum in the medium based on PW from oil fields.

#### Molecular Structure

The identification of xanthan gum was made by the technique of mass spectrometry in the IR, evaluating the biosynthesized gum through the partial identification of the molecular structure of the compounds and comparing them with a commercial xanthan gum.



Analyzing the IR spectroscopy of the gum obtained from PW of wells A and B, supplemented with sucrose and raw glycerin at a concentration of 20 g.L<sup>-1</sup> each, and commercial xanthan gum (Figure 4), it can be observed that the band characteristic of axial deformation of hydroxyl groups (OH) occurred between 3200 to 3450 cm<sup>-1</sup>. The bands around 2950 and 2850 cm<sup>-1</sup> appearing in low intensity are assigned to axial deformation of the C-H bond and CHO. The band featuring the C = O stretch of grouping ester, carboxylic acids, aldehydes and ketones appeared between 1710 and 1730 cm<sup>-1</sup> (Dumitriu; Chornet; Vidal, 1997).

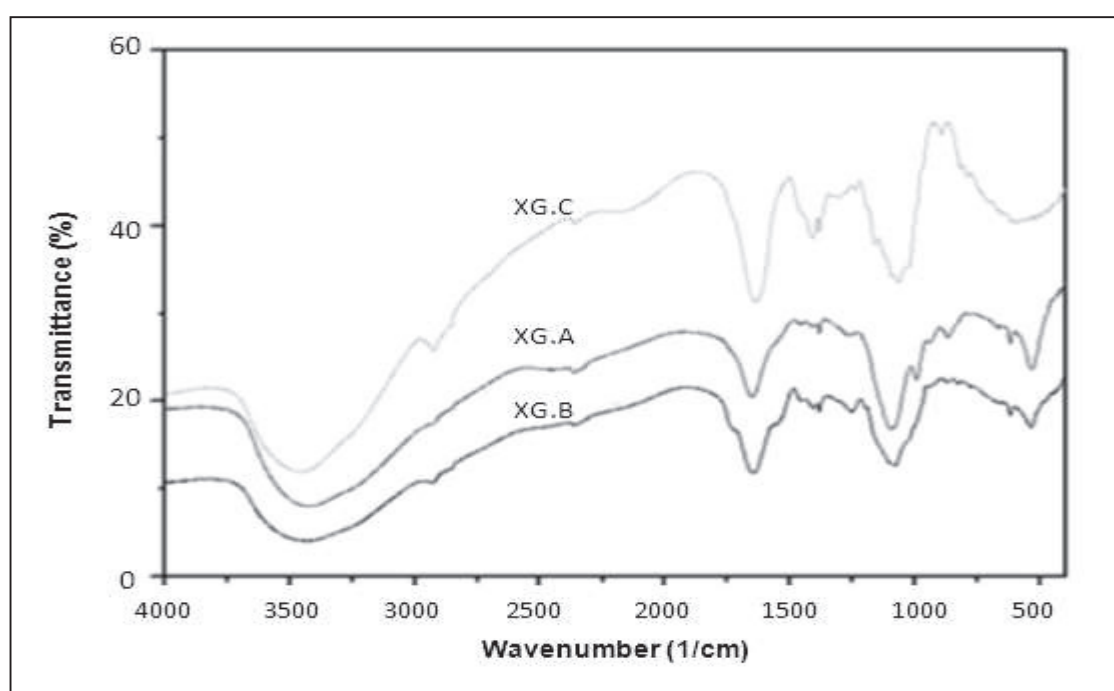


Fig. 4. Spectra in the infrared region, in KBr pellet of xanthan gum. Legend: XG.C - commercial Xanthan Gum; XG.A - Produced Xanthan Gum with residue of the well A; XG.B - Produced Xanthan Gum with residue of well B.

In 1420 to 1430 cm<sup>-1</sup> an angular deformation of C-H was observed, and between 1050 to 1150 cm<sup>-1</sup> an axial deformation of C-O was observed, typical of ethers, alcohols, phenols, fatty acids, esters and anhydrides (Silverstein; Webster, 2000)

The characteristics of functional groups found in this study were similar to those of the commercial gum. Thus, it is clear that the IR spectrum of commercial gum is very similar to that of the gums synthesized by the strain of *Xanthomonas*

*campestris* CCMICS 507 in PW from the oil industry, supplemented with sucrose and raw glycerin.

## Conclusions

It is possible to produce xanthan gum with *Xanthomonas campestris* in PW from oil fields in operational conditions of 30°C, 180 rpm, 72 h of fermentation, in sucrose supplemented medium and raw glycerin. The supplemental carbon source required varies with the wastewater source. The apparent viscosity of gums ranged from 92 to 492 cP. The xanthan exhibited pseudoplastic rheological behavior characteristic of polymer solutions of microbial polysaccharides. The Infrared Spectra of the xanthan gum obtained with PW with 2% sucrose and 2% raw glycerin synthesized by *Xanthomonas campestris* CCMICS 507 lineage were quite similar to those of commercial gum.

## Acknowledgments

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## APÊNDICE H - Fotografias das lâminas petrográficas

Inclui descrições e observações citadas no Capítulo 6 - Ensaio com amostras para testar uma técnica de MEOR (bioacidificação).

### Parte I: Fotografias de lâminas das amostras antes de ser realizado nenhum tratamento:

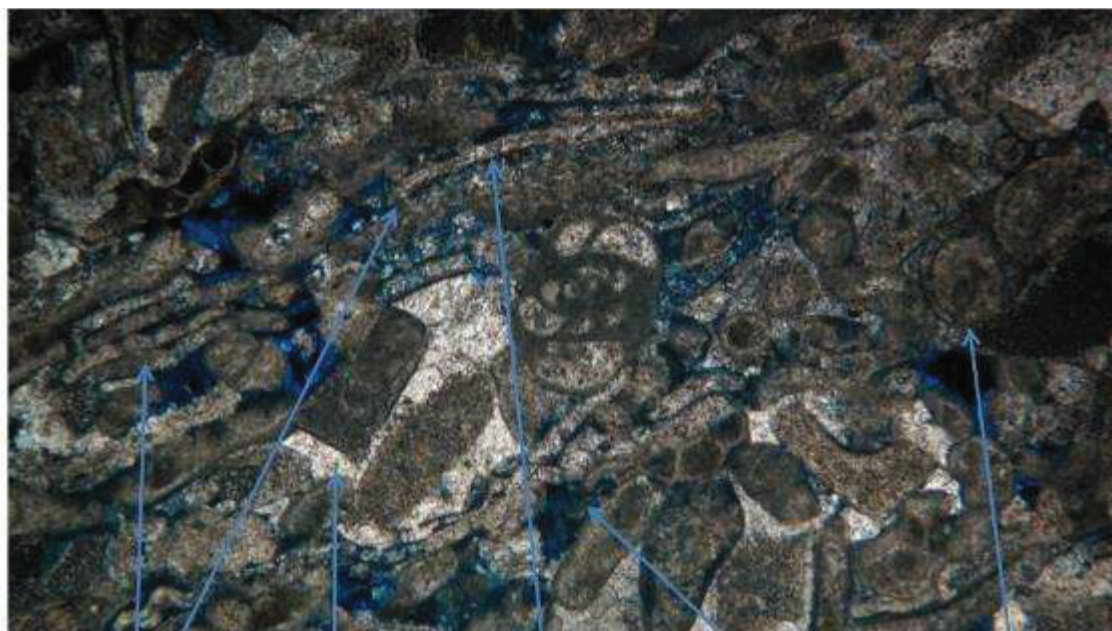


Foto #1642: amostra A, sem tratamento, 2,5x

orientação no plano  
de acamamento

cimentação de  
calcita espática

fragmento de molusco  
(pelecípode)

porosidade estimada  
em 10%-15%

oólito



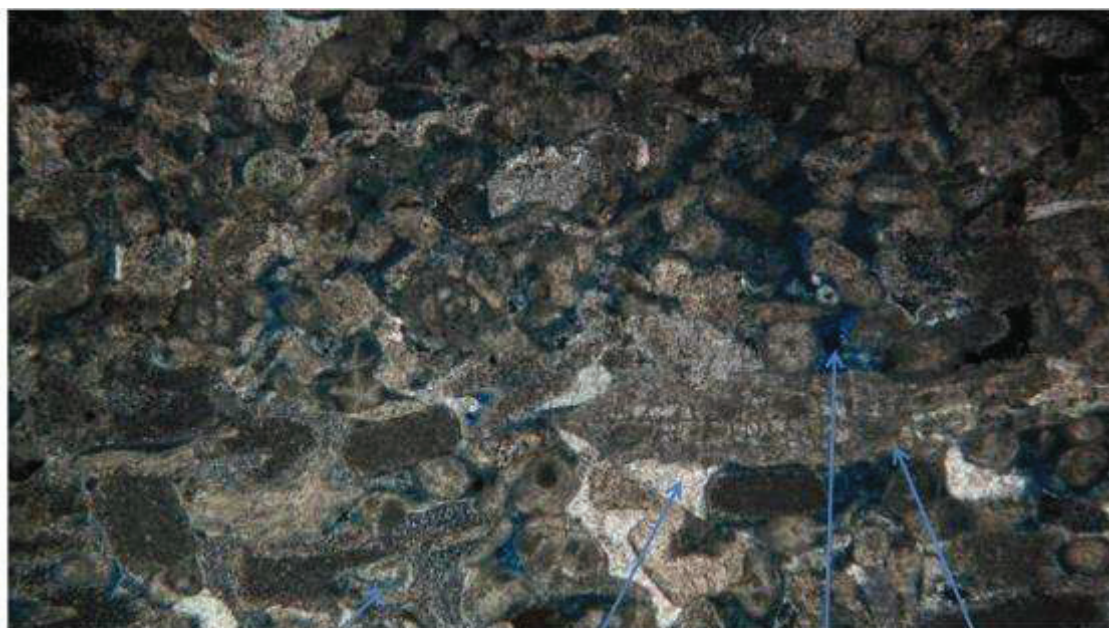


Foto #1646: amostra A, sem tratamento, 2,5x

cimentação possivelmente  
em franja fibrosa

cimentação de calcita  
espática

porosidade estimada  
em 10%-15%

braquilópode



Foto #1795: amostra B, sem tratamento, 2,5x

cimentação de  
calcita espática

oólito

cimentação possivelmente  
em franja fibrosa



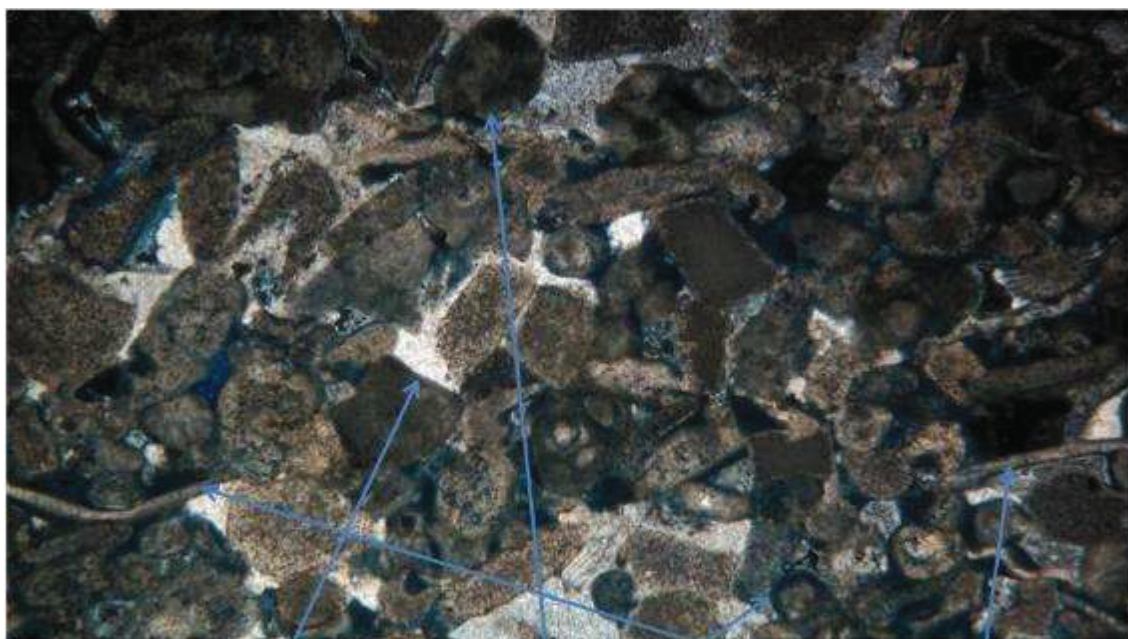


Foto #1817: amostra B, sem tratamento, 2,5x

cimentação de  
calcita espática

oolito

fragmento de molusco  
(pelecipode)

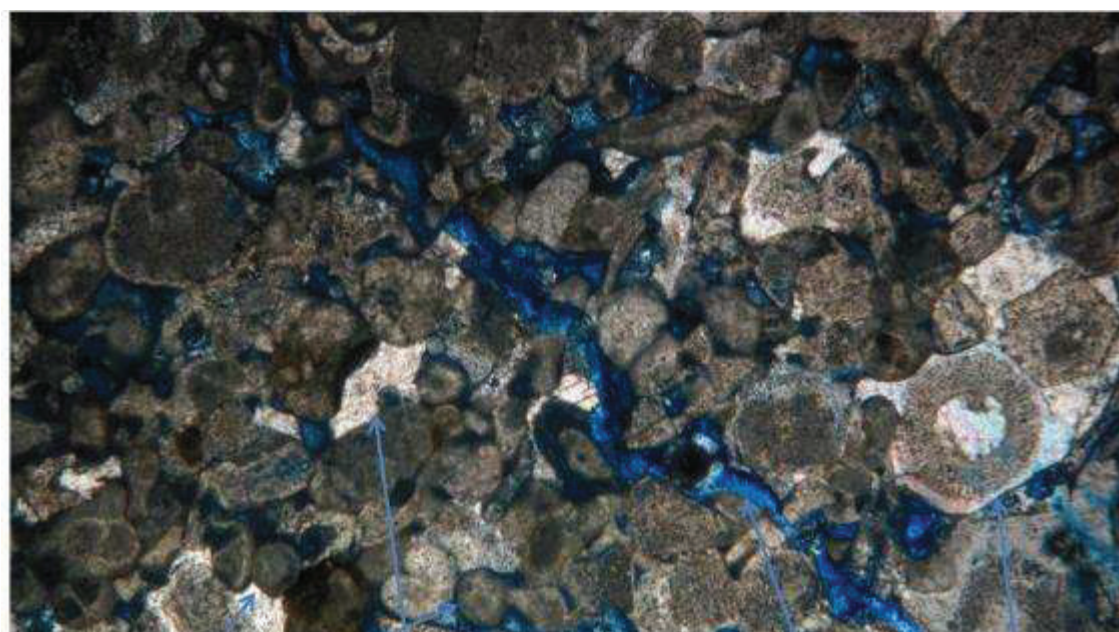


Foto #1725: amostra C, sem tratamento, 2,5x

pelecipode

cimentação de  
calcita espática

porosidade estimada  
em 10%-15%

oolito



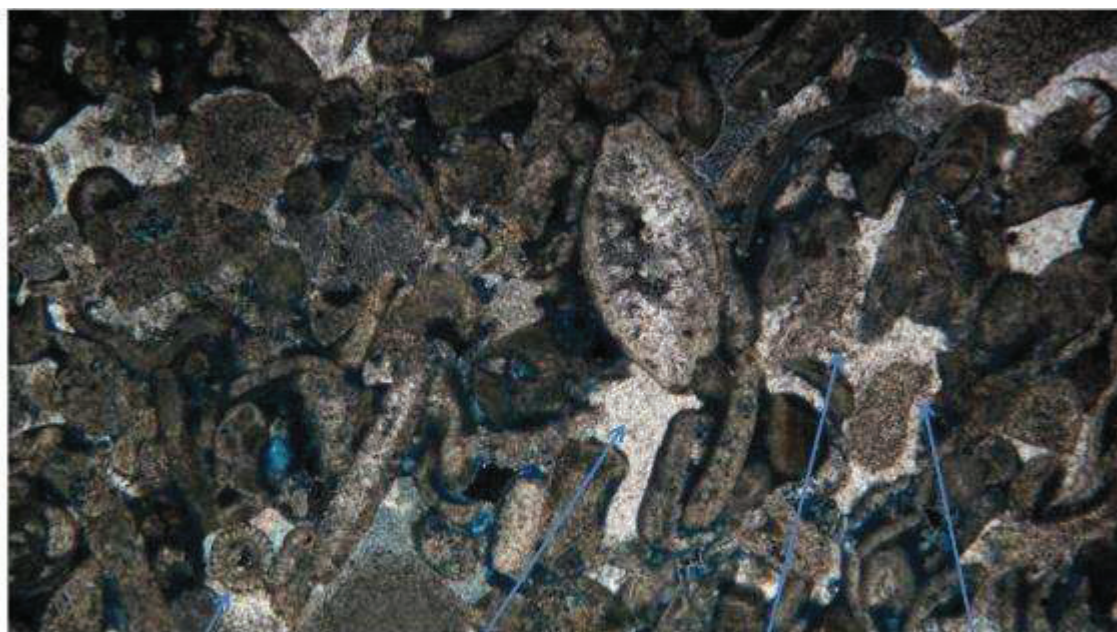


Foto #1741: amostra C, sem tratamento, 2,5x

oólito

cimentação de  
calcita espática

Recimentação(?)

cimentação em franja  
fibrosa

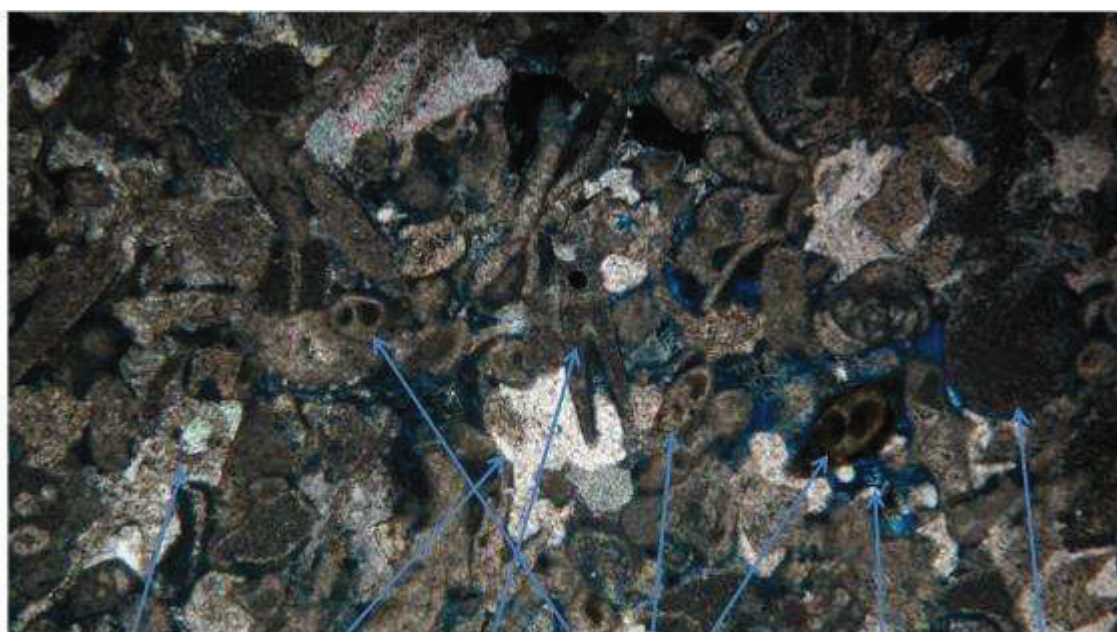


Foto #1747: amostra C, sem tratamento, 2,5x

oólito

cimentação de  
calcita espática

braquiópode

gastrópode

porosidade estimada  
em 10%-15%

oólito



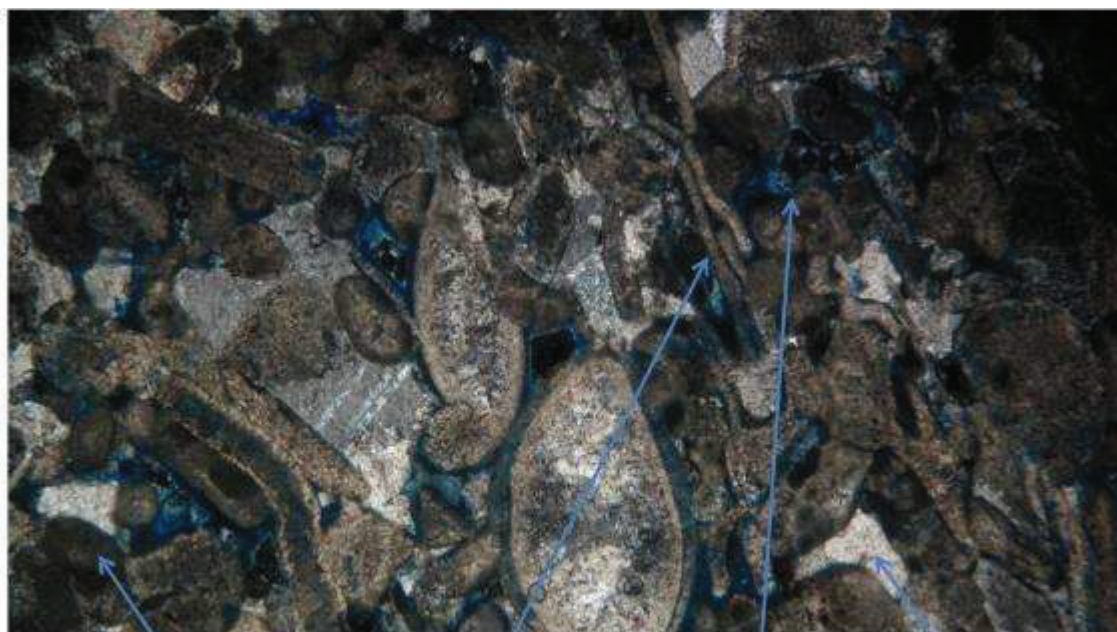


Foto #1873: amostra D, sem tratamento, 2,5x

peloide

bioclastos

porosidade estimada  
em 10%-15%

cimentação de  
calcita espática

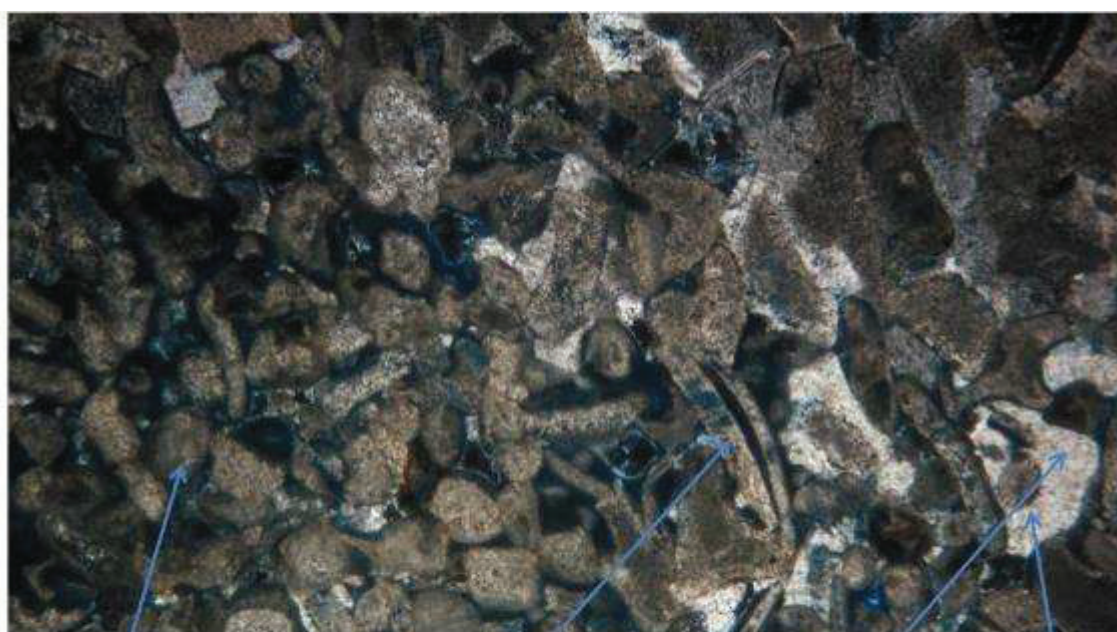


Foto #1886: amostra D, sem tratamento, 2,5x

peloide

bioclastos

cimentação de  
calcita espática

oólito

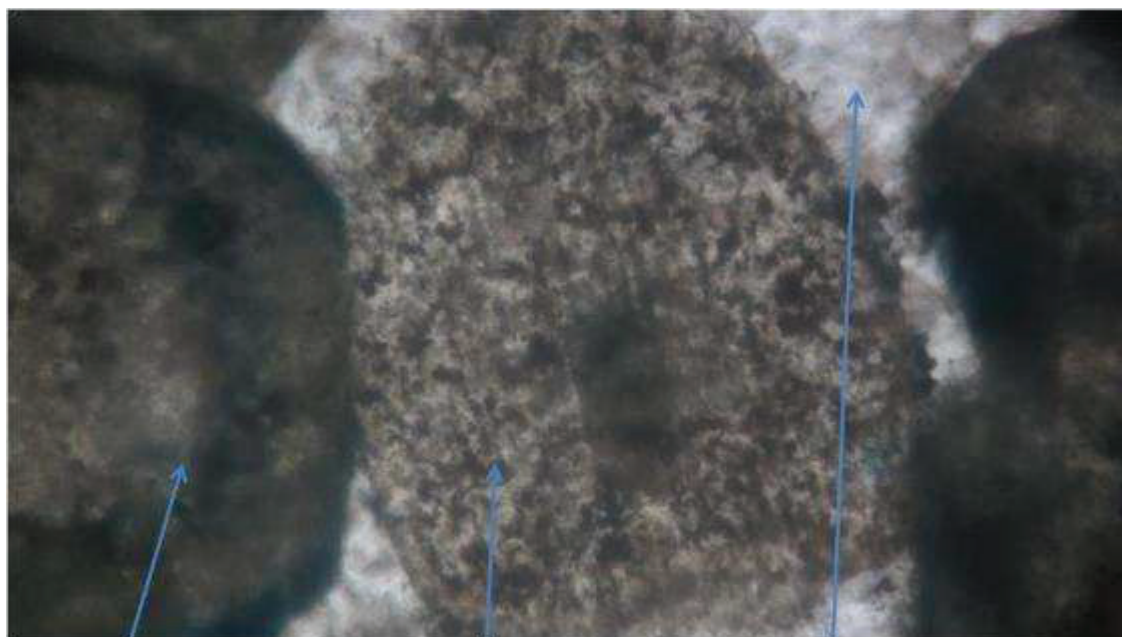


Foto #1957: Amostra A, sem tratamento, 20x

pelóide

oolito

cimentação de  
calcita espática

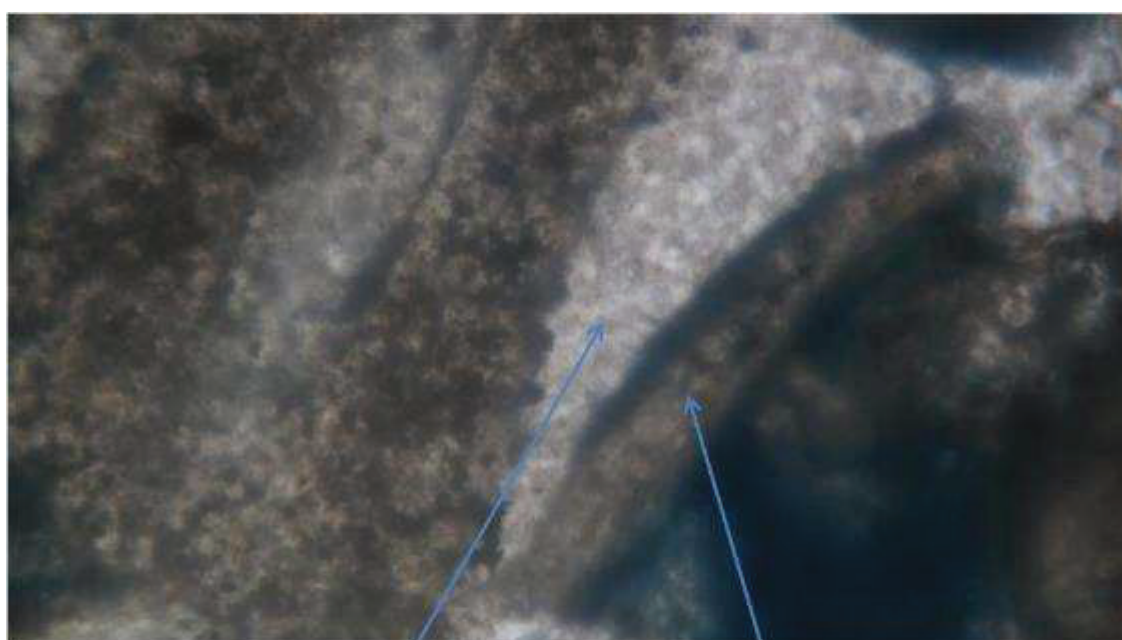


Foto #1960: Amostra A, sem tratamento, 20x

cimentação de  
calcita espática

bioclasto  
(pelecípode?)



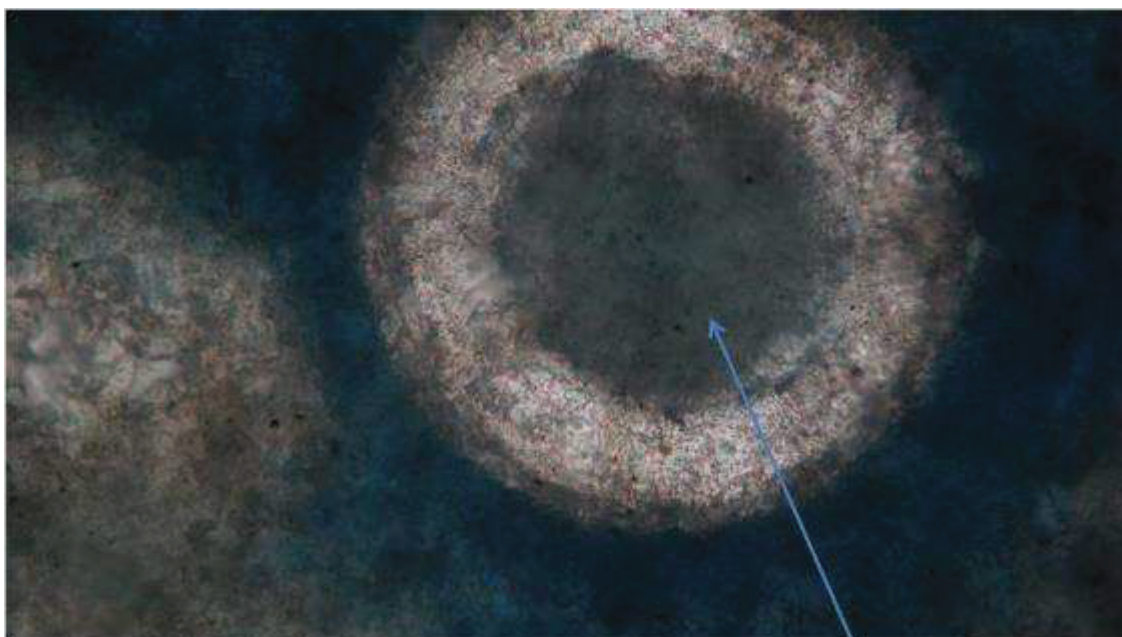


Foto #1974: Amostra A, sem tratamento, 50x

oolito



Foto #1930: Amostra B, sem tratamento, 20x

Interface de poro com  
parte de um bioclasto

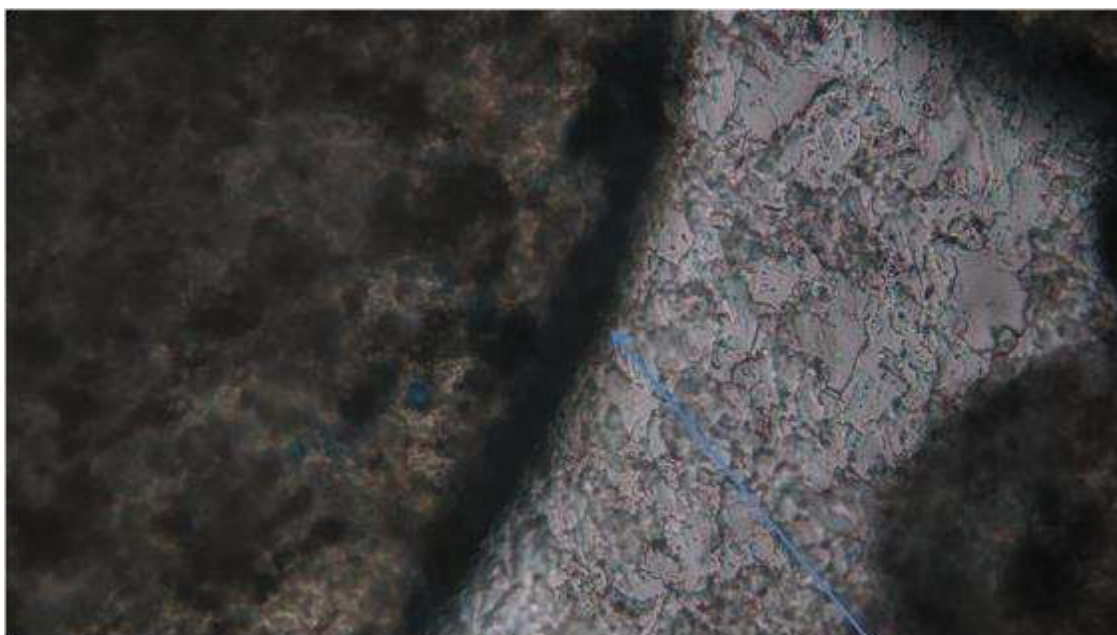


Foto #1982: Amostra B, sem tratamento, 50x

Interface de peloide com  
cimentação de calcita espática

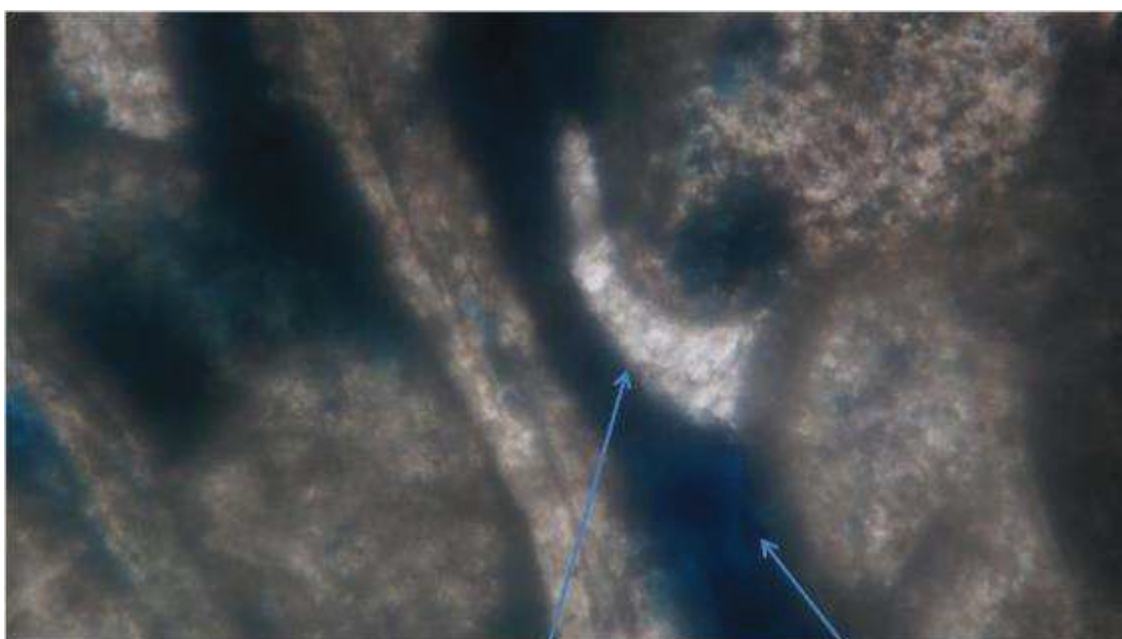


Foto #1939: Amostra C, sem tratamento, 20x

interface de poro com  
cimentação de calcita espática

interface de poro com  
parte de um bioclasto