



New Method of Rock Samples Preparation for Palynological and Palynofaciological Analysis Novo Método de Preparação de Amostras para Análises Palinológicas e Palinofaciológicas

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Abstract

This paper describes a new chemical sample preparation methodology for palynological analysis with the concentration of particulate organic material. To demonstrate the method potentiality, chemical experiments were carried out on representative rock samples composed of different lithologies, environments, and ages, from five Brazilian basins. Five sedimentary samples were taken from subsurface being four from the core and one cutting, and additionally one from outcrop, making six samples. The experiments aimed to authenticate the effectiveness of using the Fluoclor chemical reagent to replacing hydrofluoric acid (HF) ordinarily used in the preparation of palynological samples. HF acid, in Brazil, has its trade restricted and controlled by the army, making its continual acquisition impossible. Because it is a chemical compound by combining hydrofluoric acid (HF) with a small addition (~ 13%) of hydrochloric acid (HCl), it is free of this control, making routine palynological samples processing method possible. To illustrate the product efficacy, tests were performed on sediments of different ages (Paleozoic, Mesozoic, and Cenozoic) and with diverse mineralogical compositions. The data obtained attended as a comparison with the same stratigraphic intervals samples, previously processed with hydrofluoric acid (HF). The results showed that, regardless of both the stratigraphic interval analyzed and the mineralogical composition of the samples, the percentage recovery of the organic groups, as well as the marine and non-marine palynomorphs, were equivalent, thus demonstrating the reliability of the new method for chemical processing palynological samples.

Keywords: fluoclor; methodology; palynology

Resumo

Este trabalho apresenta uma nova metodologia de preparação química de amostras para estudos palinológicos com concentração de material orgânico particulado. Na comprovação da potencialidade do método, foram realizados experimentos químicos em amostras de rochas representativas de diferentes ambientes e idades, provenientes de cinco bacias brasileiras. Foram selecionadas cinco amostras de subsuperfície, sendo 4 amostras de testemunho e uma de calha, além de uma amostra de afloramento. Os experimentos tiveram como objetivo comprovar a eficácia da utilização do reagente químico Fluoclor em substituição ao ácido fluorídrico (HF), usualmente utilizado em preparação de amostras palinológicas. O ácido HF, no Brasil, tem sua venda restrita e controlada pelo exército, inviabilizando sua aquisição constante. O Fluoclor por se tratar de um produto químico composto pela combinação de ácido fluorídrico (HF) com uma pequena adição (~13%) de ácido clorídrico (HCl), torna-o livre desse controle, viabilizando o processamento rotineiro de amostras pelo método palinológico. Visando ilustrar a eficácia do produto, testes foram realizados em sedimentos de diferentes idades (paleozoica, mesozoica e cenozoica) e com composições mineralógicas distintas. Os dados obtidos serviram de comparação com amostras dos mesmos intervalos estratigráficos, previamente processadas com ácido fluorídrico (HF). Os resultados mostraram que, independente tanto do intervalo estratigráfico analisado quanto da composição mineralógica das amostras, a recuperação percentual dos grupos orgânicos, bem como dos palinomorfos marinhos e não marinhos foram equivalentes, demonstrando assim a confiabilidade no emprego do novo método para processamento químico de amostras palinológicas.

Palavras chave: fluoclor; metodologia; palinologia

1 Introduction

Researchs in the palynological field has long been a significant part of the oil, gas and coal deposits investigations. As a result, sample processing in this area is of crucial importance as inadequately performed can convert an operative palynological sample into a sterile one.

The literature is rich in palynological and palynofaciological processing methodologies articles. Some often highlight sophisticated equipment, microwaves, special large-scale sample digestion devices, hot acid attacks, or sample processing equipment in controlled environments, etc. (Poulsen *et al.*, 1990; Simes & Wrenn, 1998).

Certainly, this is not the scope of the present work, which only intends to demonstrate that Fluoclor acid treatment can be an advantageously substitute for the hydrofluoric acid method of standard processing. Researchers yearning to improve their palynological and/or palynofaciological processing techniques should learn the articles published by Uesugui (1979), Quadros & Melo (1987), Mendonça Filho, J.G. (1999) and Oliveira *et al.* (2004) published in Brazil and the international papers from Batten & Morrison (1983), Tyson (1995), Wood *et al.* (1996), and Traverse (2008) mainly.

2 Materials and Methods

To determine the new method potentiality several tests were performed, and as a demonstration. Examples are presented below and all the methodological steps performed on six samples from five Brazilian sedimentary basins. There was a concern to obtain samples of both outcrops and drill holes with strict stratigraphic control and covering distinct geological periods. Thus, sedimentary samples from Paleozoic, Mesozoic, and Cenozoic ages, belonging to the Paraná (well 9-PPG-2-PR), Parnaíba (wells 9-PAG-6-MA and 1-UR-05-PI), Recôncavo (well 9-FBA-79-BA), Araripe (well 4-BO-1-PE), and Taubaté (outcrop- Coordinated: 220 56 ' - 59.8 "S and 450 32' - 29.9" W) basins, were selected.

2.1 Methodology of Chemical Sample Preparation

All samples were processed in the Palynomacerals Laboratory at UERJ via the following pro-

cedures. Crushed approximately 40 grams of each sample in pieces of *c.* 2.0mm in diameter, and placed it in labeled polypropylene beaker. Following, test sample with a few drops of 10% HCl. If it effervesces, add enough hydrochloric acid (37% HCl) covering the entire sample. This first attack, with a minimum duration of two (2) hours, aims to eliminate the possible carbonate fraction present in the samples.

Once the attack is over, wash the samples with distilled water three times until the neutralization. At each washing step, a 10 μ m mesh sieve is required for the supernatant liquid disposal to retain mainly the algal material, which may have remained suspended in the liquid. Subsequently, add the fluoclor acid twice the sample volume to remove the silicates. During the first two hours with fluoclor, it is necessary to shake the samples with polypropylene drumstick for better homogenization of the attack. Next, after 24 hours, repeat the sample neutralization operation.

Then, sieve the residue with 200 μ m opening mesh discarding the material retained in it. After that, transfer the sieving residue to a glass beaker and attack it with a hot 37% HCl in sufficient quantity to cover the material. Heating remains for approximately two hours in a hot plate at 40 °C, to remove the silica gel formed during the previous step chemical reactions. After the silica gel removal and neutralization of the medium with distilled water, transfer the residue to a 50 ml falcon tube and completed with zinc chloride (ZnCl₂) of 1.9 to 2.0 density. After 24 hours in decantation, collect the remaining residue (kerogen) with a pipette, transfer it to a new 50ml falcon tube, and complete with 70% alcohol to eliminate ZnCl₂. After the complete residue washing, make successive beating processes in a watch glass, for a more significant organic material concentration. Sieve the remaining residue in a 10 μ m mesh for palynomorphs concentration and subsequent mounting the palynological slide.

Finally, collect 2 to 3 drops from the drum residue to make the organopalynological slides. Make the slides using a hot plate with a temperature around 30 °C for drying, and Norland for fixing (figure 1).

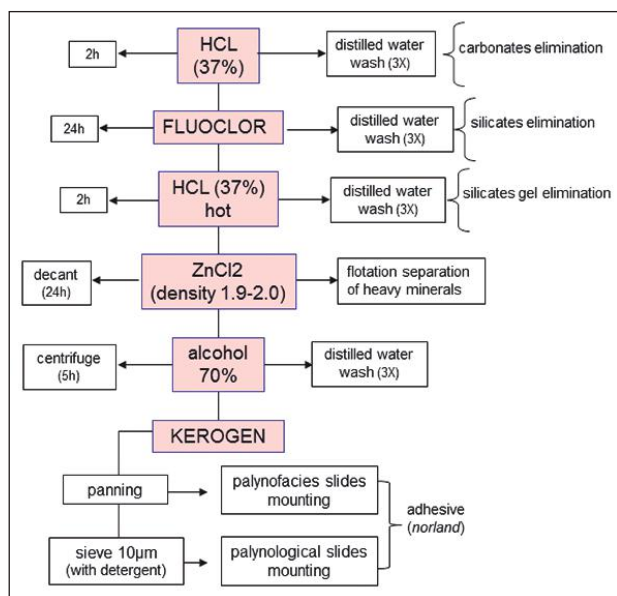


Figure 1 Detailed flow-chart illustrating all steps for extracting palynomorphs from rock samples using fluoclor acid.

2.2 Particulate Organic Content Characterization

The characterization of the organopalynological association was based on the qualitative and quantitative analyses of the recovered particulate organic material from the different sampled lithologies.

Type identification, quality, and preservation of the organic material were obtained by visualization under optical microscopy in the transmitted light and fluorescence mode.

Representing the relative frequencies of organic groups the Tyson (1995) methodology was adopted here, with the counting of 300 organic particles, including marine and non-marine elements.

According to Tyson (1995), this representativeness ideally reflects all the organic components included in the sample.

For statistical representation was considered the grouping of the following organic elements: amorphous organic material, phytoclasts (opaque, non-opaque, cuticular tissue, tracheids), palynomorphs (pollen grains, spores, acritarchs, and chitinozoans), and marine and continental algae.

3 Results

The results obtained with the new method application proved to be quite satisfactory, consid-

ring the action of fluoclor to the hydrofluoric acid equivalence.

The equality of the techniques was confirmed by visual analysis under optical microscopy in white light and fluorescence, taking into account the quality and preservation of organic matter, as well as statistical data obtained through the percentage of organic groups present. It was also observed that the new method provided a greater recovery of paleomicroplankton.

The results obtained from the six investigated samples are shown in figures 2 to 6 and revealed the potentiality of the new method both in the concentration of organic material and in the percentage values obtained in all samples.

3.1 Paraná Basin

A core sample tested from Paraná Basin belongs to the well 9-PPG-2-PR, located in the Ponta Grossa Arc region, in the Apucarana Sub-Basin.

The sample comprised of siliceous shales from the Ponta Grossa Formation aged as Lower Devonian.

Both methods presented significant recovery of marine paleomicroplankton (chitinozoans, acritarchs and prasinophytephycomata) representatives, besides allochthonous elements (phytoclasts, cuticular tissues, and spores). However, there is a small increase in the percentage recovery of the autochthonous elements when using the fluoclor reagent. (figure 2).

3.2 Parnaíba Basin

In the representations of the experiments carried out in the Parnaíba Basin, the selected two core samples are one of Permian age and another from the Lower Cretaceous. Figure 3 presents the results of the Permian (Pedra de Fogo Formation) representative sample, belonging to the 1-UR-05-PI well and composed by shales with fine sandstone lenses.

The result shows a higher recovery of palynomorphs, mainly baccate pollen grains, with the application of fluoclor, and after the beating stage.

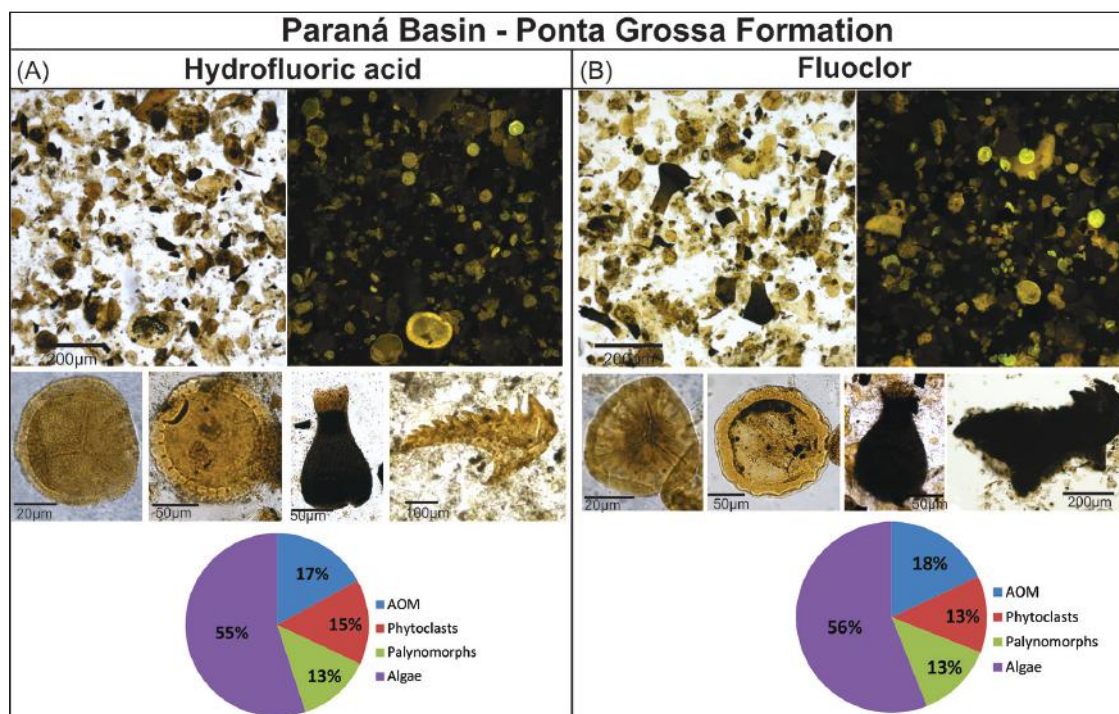


Figure 2. Comparative photomicrographs between chemical treatments with HF (A) and Fluoclor (B) in samples from the Ponta Grossa Formation - Devonian of the Paraná Basin. Observe (on the graphics) the highest percentage recovery of autochthonous constituents (MOA + Algae) on the Fluoclor attack.

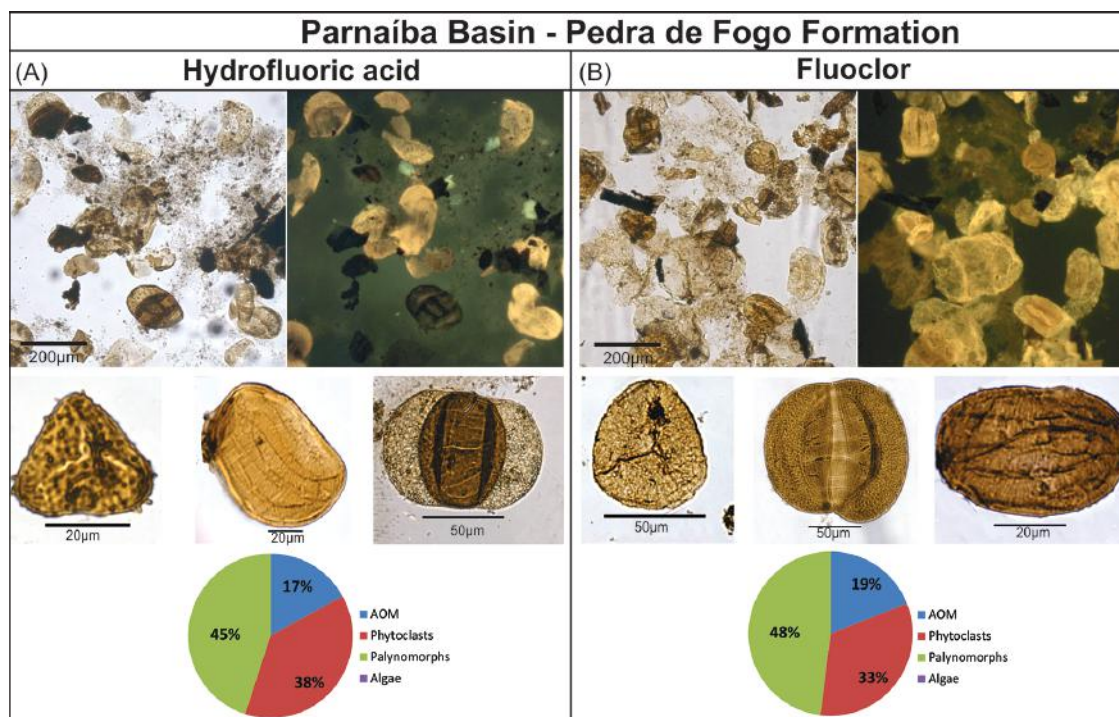
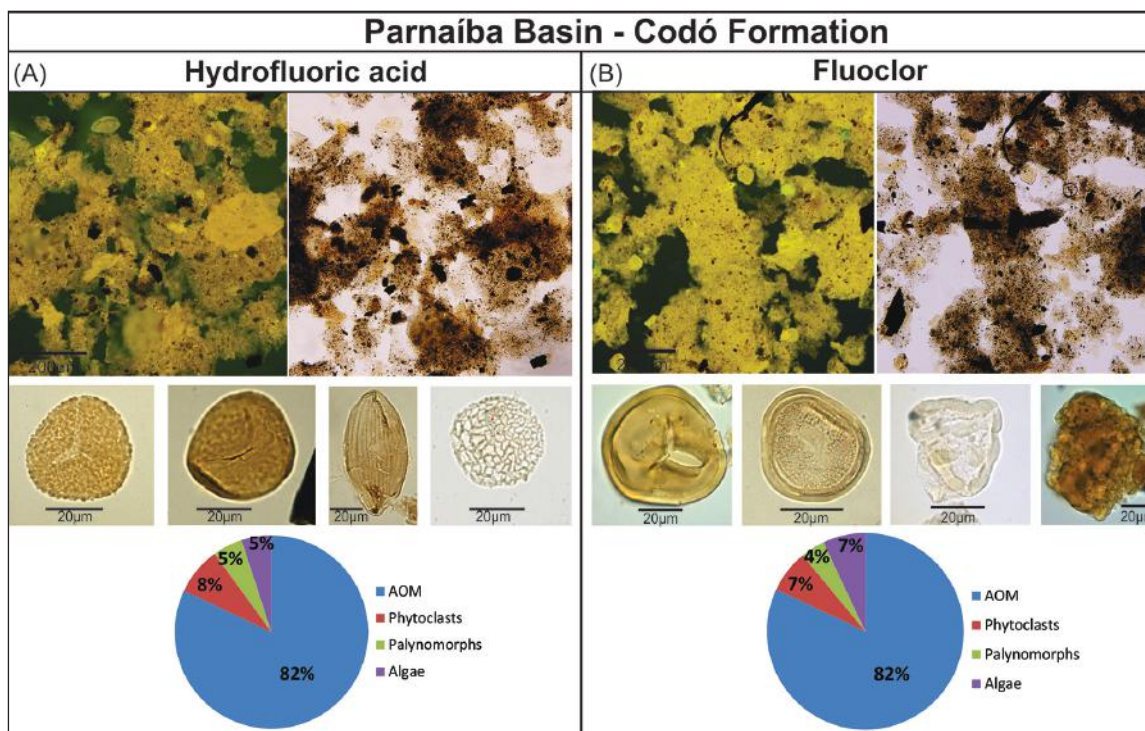


Figure 3. Comparative photomicrographs between chemical treatments with HF (A) and Fluoclor (B) in samples from the Pedra de Fogo Formation - Permian of the Parnaíba Basin. Observe (on the graphics) the highest percentage recovery of bissetates pollen grains and MOA on the Fluoclor attack.

To exemplify the interval corresponding to the Lower Cretaceous (Codó Formation) in the Parnaíba Basin, the core sample selected is a bituminous and limestone shale that comes from the well 9-PA-

G-6-MA. The result shows that the new method is similar to the traditional one and, even subtly, is possible to observe a higher recovery of algal elements (figure 4).

Figure 4. Comparative photomicrographs between chemical treatments with HF (A) and Fluoclor (B) in samples from the Codó Formation - Lower Cretaceous of the Parnaíba Basin. Observe (on the graphics) a higher percentage recovery of the algal elements on the Fluoclor attack.



3.3 Recôncavo Basin

The selected sample from the Recôncavo Basin is a core sample from well 9-FBA-79-BA located in the NE portion of the Bahia State, in the city of Aramari. The sampled level corresponds to Lower Cretaceous sediments (Pojuca Formation) composed of shales with intercalations of fine to medium sandstones and deposited in a fluvial-deltaic environment. In figure 5 is possible to observe an equivalence of the percentage values of organic groups in both methods, with a domain of amorphous organic material.

3.4 Araripe Basin

To represent the Araripe Basin, the selected sample comes from well 4-BO-1-PE, in strata of the Santana Formation (Lower Cretaceous). The cutting sample consists of shales with limestone and sandstone intercalations, deposited in a fluvial-lacustrine environment. The data obtained show a very subtle difference in the percentage of the algal group and phytoclasts (~ 1%) (Figure 6).

3.5 Taubaté Basin

The selected sample comes from an outcropping section located in the Tremembé city- SP Sta-

te, more specifically in Santa Fé Extractive Industry. The results show a good kerogen recovery with organic matter elements represented by phytoclasts, cuticular tissues, fungi, pollen grains, spores, lacustrine algae and with higher representation of amorphous organic material. (figure 7).

4 Discussion

The results of the experiments performed with the two acids (HF and Fluoclor) were quite equivalent. Fluoclor-processed samples demonstrated efficacy in both the concentration of organic content (kerogen) and inorganic elimination.

Allied to this it was found that the new method provides a higher concentration and recovery of paleomicroplankton (MOA, marine and continental algae) representatives, demonstrating that not only the fluoclor is equivalent in its action to hydrofluoric acid but also provides more comprehensive recovery of palynomorphs.

The results confirmed the efficacy and reliability of the new method and that it can be applied to samples with different mineralogical compositions, and in most stratigraphic intervals.

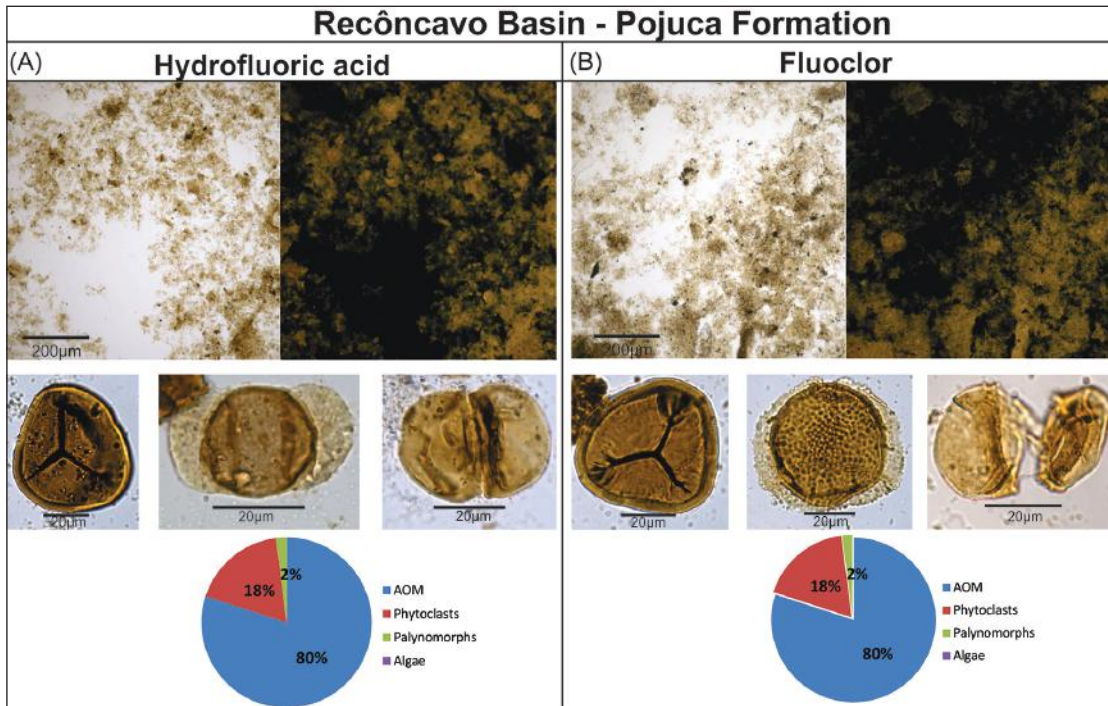


Figure 5. Comparative photomicrographs between chemical treatments with HF (A) and Fluoclor (B) in samples from the Pojuca Formation - Lower Cretaceous of the Recôncavo Basin. Observe the percentage equivalence in the recovery of the organic groups with the application of the two acids (HF and Fluoclor).

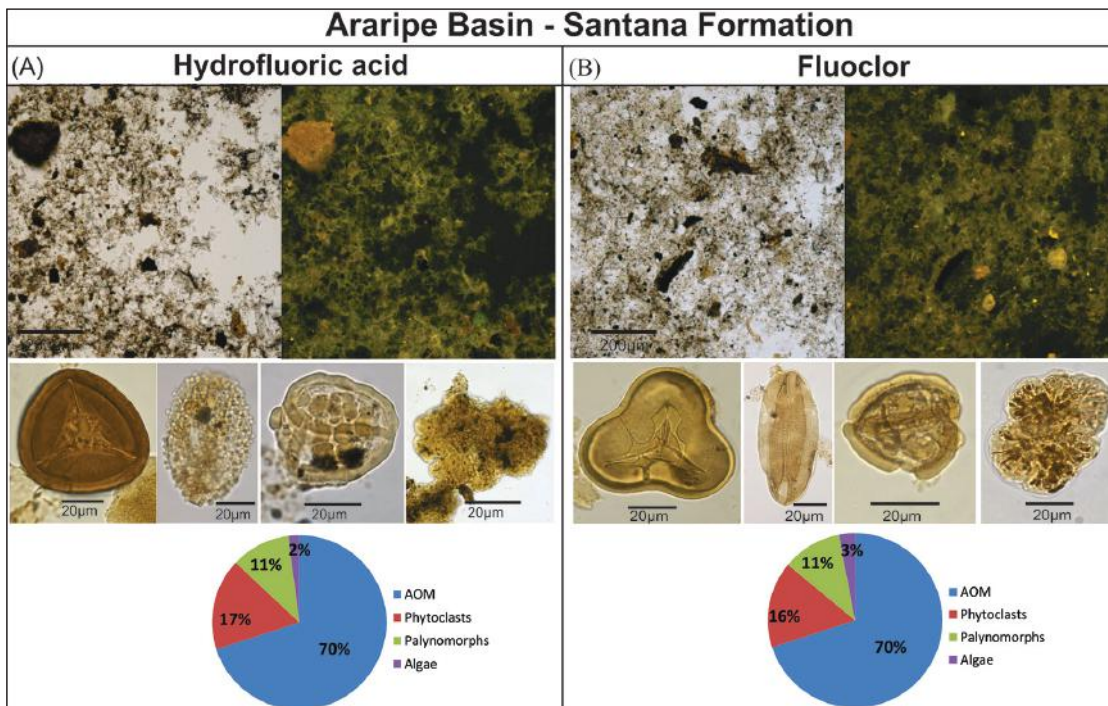
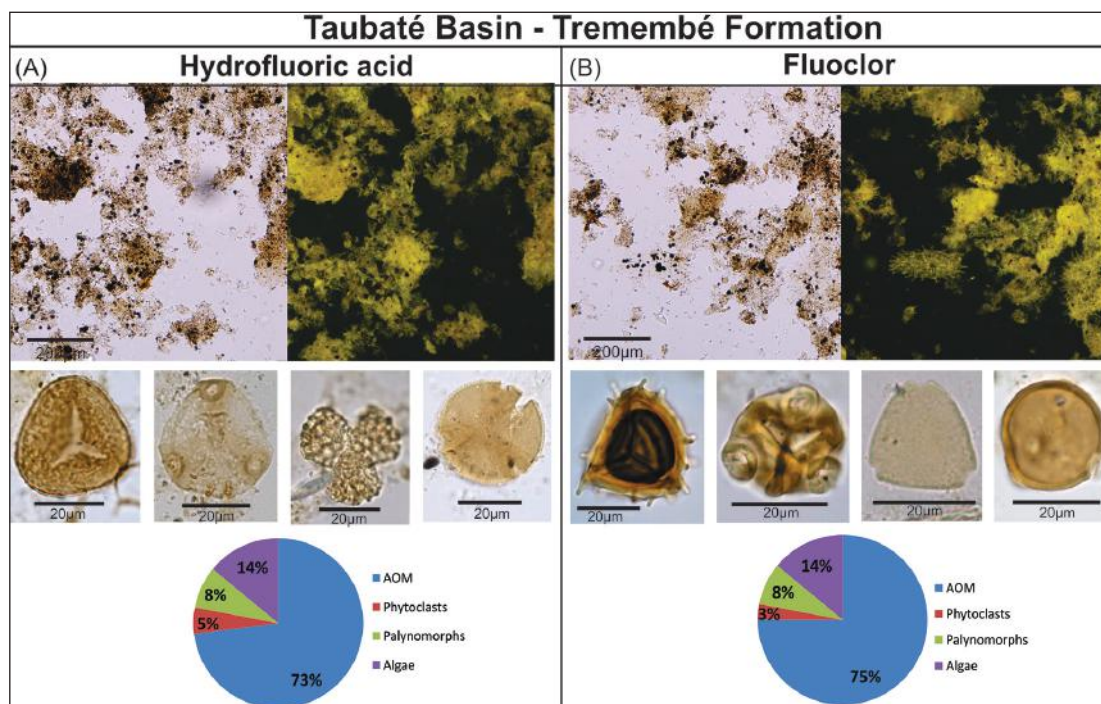


Figure 6. Comparative photomicrographs between chemical treatments with HF (A) and Fluoclor (B) in samples from the Santana Formation - Lower Cretaceous of the Araripe Basin. Observe a slight increase in algae recovery is when attacked with Fluoclor.

Figure 7. Comparative photomicrographs between chemical treatments with HF (A) and Fluoclor (B) in samples from the Taubaté Formation - Oligocene of the Araripe Basin. Observe higher recovery of amorphous organic material when attacked with Fluoclor.



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