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SOURCE ROCK CHARACTERIZATION OF PARANÁ BASIN, BRAZIL: SEM AND XRD STUDY OF IRATI AND PONTA GROSSA FORMATIONS SAMPLES

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Resumo – O principal objetivo deste trabalho é a caracterização do conteúdo mineral das rochas geradoras da Bacia do Paraná utilizando as técnicas de Microscopia Eletrônica de Varredura e Difractometria de Raios-X. O material amostrado foi coletado em afloramentos, cavas de mineração e sondagens da CPRM e do DNPM. Por ser uma técnica qualitativa e semi-quantitativa a Microscopia Eletrônica de Varredura é aplicada para quantificar a matéria mineral e identificar sua morfologia utilizando a Espectroscopia de Dispersão de Energia. As amostras analisadas indicaram que o ataque ácido realizado nas amostras não é totalmente efetivo na separação das fases minerais da matéria orgânica presentes nas rochas geradoras, possivelmente porque a matéria orgânica cobre alguns minerais bloqueando o efeito do ataque ácido. Após a acidificação observa-se que óxidos e sulfetos aumentam percentualmente enquanto carbonatos e silicatos diminuem. Também foi observado que as amostras que não passaram pelos ataques ácidos são essencialmente constituídas de fases minerais ricas em silicatos, carbonatos e sulfetos. Os resultados obtidos mostram que nos querogênios existem fases minerais inorgânicas e que nas fases inorgânicas existe uma boa correlação de: C, Ca e Mg com Carbonatos; Al, Si e K com Aluminossilicatos e Fe, Co, Cu, Zn com sulfetos.

Palavras-Chave: Bacia do Paraná, MEV, XRD.

Abstract – This work aims mainly at the characterization of the mineral content in source rocks of the Paraná Basin by means of Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) techniques. The sample was collected from outcrop, surface mines and core from exploration boreholes and provided by the Geological Survey of Brazil and the National Department of Mineral Production. The applicability of SEM technique is for semi quantitative and qualitative minerals source rocks studies and identification of their morphology using Energy Dispersion Spectroscopy (EDS) and image mode. The samples analyzed indicated that the acid attack is not totally effective for separating the mineral phases from the organic matter, possibly because the organic matter surrounds the mineral phases, blocking the effect of acid attack. It was observed a percentual increase in the amount of oxides and sulfides, and a decrease in the amount of silicates and carbonates. The samples which have not been under acid attack show that the source rocks are essentially formed by silicates, carbonates and sulfides. The results obtained from the kerogens presents exist inorganic phases and the presence this inorganic phases shows a correlation between: C, Ca, Mg (carbonates); Al, Si, K (aluminosilicates); Fe, Co, Cu, Zn (sulfides).

Keywords: Paraná Basin, SEM, XRD.

1. Introduction

All sedimentary rocks are composed of a mineral matrix and varying amounts of organic matter that, depending on kerogen type, is oil prone (type I, II), gas prone (type III) or has no hydrocarbon potential at all (type IV). Usually sedimentary rocks of fine granulometry are characterized by a relatively high organic matter content, related to their formation in a low energy depositional environment. The study of these rocks involves a complex preparation of samples. It is necessary to separate the organic portion from mineral matter by using HCl and HF to eliminate carbonate, quartz and clay minerals.

This work aims mainly at the characterization of the mineral content in source rocks of the Paraná Basin by means of Scanning Electron Microscopy (SEM) techniques and X-Ray Diffraction (XRD).

This organic matter concentration method is many times inefficient, resulting in a mixture of kerogen and mineral matter "contamination" in the enriched kerogen. This contamination and the possible transformations of the mineral matter types during the preparation of the Irati and Ponta Grossa formation samples led to questions on the natural relationships between the generated kerogens and its mineral matter constituents.

Earlier electron microscopy based studies of sedimentary organic materials have usually been restricted to the examination of organic particles, separated from mineral matrix by treatment with HF (hydrofluoric acid) and HCl (chloridric acid), visualized using secondary electron imagery (SEI). Such images convey detailed information of the structure and morphology of 3-dimensional objects (Scott and Collinson, 1978; Davis et al, 1986).

The use of Scanning Electron Microscopy (SEM) in the study of inorganic components of sedimentary rocks is well documented (Welton, 1984, Trewin, 1988; Harrison C.H. 1991; O'Brien and Slatt, 1990), but apart from palynological studies, previous applications of SEM to the analysis of the organic components of sediments are limited.

2. Material and Methods

The sample material was collected from outcrop, surface mines and core from exploration boreholes and provided by the Geological Survey of Brazil and the National Department of Mineral Production.

2.1 Sample Preparation for SEM analysis

For the Scanning Electron Microscopy-Energy Dispersive analysis the following procedures were executed: The samples were fixed on a stub and carbon and gold coated, using a Sputter Coater (SCD 005/BALTEC) with approximately 20 nm of thickness, in order to eliminate any undesirable charge effects during SEM observations. After these procedures it was possible to do the microscopy analysis. The instrument used in this study was standard Scanning Electron Microscope Philips model XL30. The images used in this work were obtained by back-scattered electron mode, with a primary scanning beam of voltage of approximately 20 kV.

2.2 Theory: Scanning Electron Microscopy (SEM)

In the SEM, a sample is placed in a Chamber under vacuum and exposed to a focused beam of electrons, which scans over the surface of the specimen. These electrons, known as primary electrons, undergo a number of elastic and inelastic collisions with the atomic nuclei of the surface of the sample. The collisions result in the generation of a number of different types of changed particle and electromagnetic radiation, including secondary electrons, back-scattered electrons and X-rays.

Inorganic inclusions on the surface of source rocks specimens were analyzed using a Scanning Electron Microscopy (SEM) equipped with an -Energy dispersive X-ray (EDX) detector and back-scattered electron (BSE) detector. This technique can be used to determine and distinguish materials and trace element occurrences in surfaces of source rocks specimens. The reason why the SEM is capable of finding many trace elements occurrences is because the brightness of the back-scattered electron image (BSEI) is determined largely by average atomic number of the material under the electron beam. As a result, phases rich in heavy trace elements appear much brighter than normal silicate and sulfide minerals in the source rocks and can be readily located for standard EDX analysis in the SEM. The main advantage of the SEM-EDX technique is that information is obtained on the chemical association of the trace elements, from which the mineral occurrence can often be deduced.

2.3 X-Ray Diffraction (XRD)

X-ray powder diffraction patterns were obtained with a X-ray diffractometer (D5000 Siemens-Bruker-AXS, 40kV, 25mA, Cu K α radiation, diffract plus ® Siemens-Bruker-AXS software was used for data treatment), using steps

of $0.02^\circ 2\theta$ with a counting rate of 1s/step in a interval of 2 to 72 degrees for the bulk samples of coal and after acid attack.

3. Results and Discussion

The results obtained so far indicate that the SEM can be used for the identification of the main mineral phases of a source rock (generally fine granulometry and constituting in its great majority of polymorphous of silic, carbonates, amorphous, oxides and sulfites), as well as their quantification in the kerogens. A clear difference between mineral matter inclusion and organic matter was possible. In figure 1a and 1b the mineral inclusion can be observed as framboidal and cubic pyrite, respectively confirmed by EDS analysis.

In figure 2a and 2b it was observed carbonates such as Calcite (CaCO_3), Dolomite (CaMgCO_3)₂ shown in Figure 3a and Ankerite ($\text{Ca(Fe}^{++}, \text{Mg, Mn)(CO}_3)_2$). The great majority of these materials are completely destroyed by the action of the chloridric acid, replaced by a "composed carbonated amorphous mass" rich in heavy metal elements such as Chromium (Cr), Lead (Pb), Niobium (Nb), Titanium (Ti), Platinum (Pt), Manganese (Mn) and Antimonium (Sb).

In samples analyzed with fine granulometry it was possible to characterize the elements of each mineral phase, as well as the clay-minerals which, along with kerogen constitute the matrix of the analyzed rocks. The analyses also showed that the kerogen can involve some mineral grains, blocking the acid attack.

After the acid attack it was observed the oxides presence where the most common is the rutile (TiO_2) which probably must have been set free of the quartz structure when it was destroyed by the action of the acids and organic carbonate amorphous shown in Figure 3b.

In the samples that underwent thermal alteration by eventual intrusions, usually constituted of dolerite we observed the presence of platinoids, talc and serpentine that appear associated to remaining quartz, carbonates and k-feldspates disperse in the kerogen.

X-ray diffraction analysis shows in figure 4 that the clay minerals (illite, kaolinite) and quartz are dissolved with the relative concentration of oxides such as rutile, molibdenite and pyrite. Moreover, we observe that the carbonates are also attacked by the acids, remaining a carbonated matrix that absorbs some heavy minerals such as Cr, Zn, F, Ba, Cu, and Fe.

4. Conclusions

A range of techniques, including X-ray diffraction and electron microscopy, may be used to evaluate the nature of mineral matter in source rocks. Overall, this study illustrates that the Scanning Electron Microscopy techniques of Backscattered Electron Scanning (BSE) and microanalysis represent important tools in the field of organic geochemistry.

The results offer an insight into the relationship between the petrological characteristics of a sample and its geochemistry. It was possible by means of Scanning Electron Microscopy (SEM) to locate sedimentary organic matter in the source rock followed by direct analyses for elemental content using BSE and EDS.

This study is important because it shows that the SEM and XRD techniques can be used for the identification of the main mineral phases of a source rock (usually of fine granulometry and constituted mainly by clay minerals, silic polymorphous, carbonates, oxides and sulfites). Furthermore, we can identify the mineral phases remaining after the acid attack in the kerogen.

The analyzed samples indicated that the acid attack is not totally effective in separating the mineral phases from the organic matter, possibly because the organic matter surrounds the mineral phases, blocking the effect of acid attack. It was also observed a perceptual increase in the amount of oxides and sulfides, and a decrease in the amount of silicates and carbonates. The samples, which have not been under acid attack, show that the source rocks are essentially formed by silicates, carbonates and sulfides.

The results obtained from the kerogens show an association with V and Ga, whereas the remaining inorganic phase shows a correlation between: C, Ca, Zn, Fe, Mo and Mg (carbonates); Al, Si, Ti and K (aluminosilicates); Fe, Co, Cu, Mo, Mn, Ba, Cl, Zn, (sulfides).

The results from SEM analyses are consistent with the mineralogical data obtained from X-ray diffraction, which showed that pyrite and carbonates are common.

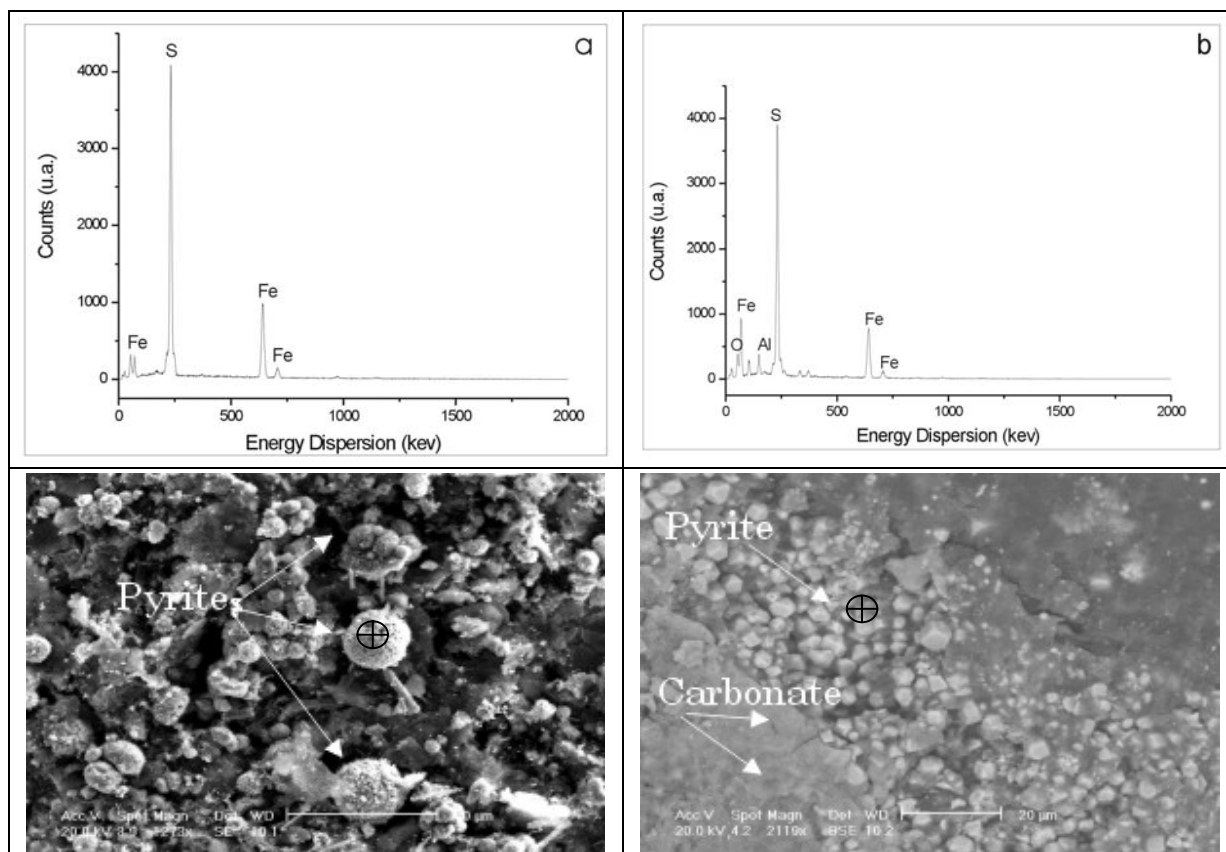


Figure 1(a): EDS characteristic of the sample 04-054 and SEM micrographs showing the framboidal pyrite in Irati sample number 04-054. 1(b) EDS characteristic of the sample 04-055B and SEM micrographs showing pyrite cubic and carbonates amorphous. $\oplus$ = Analyzed Point

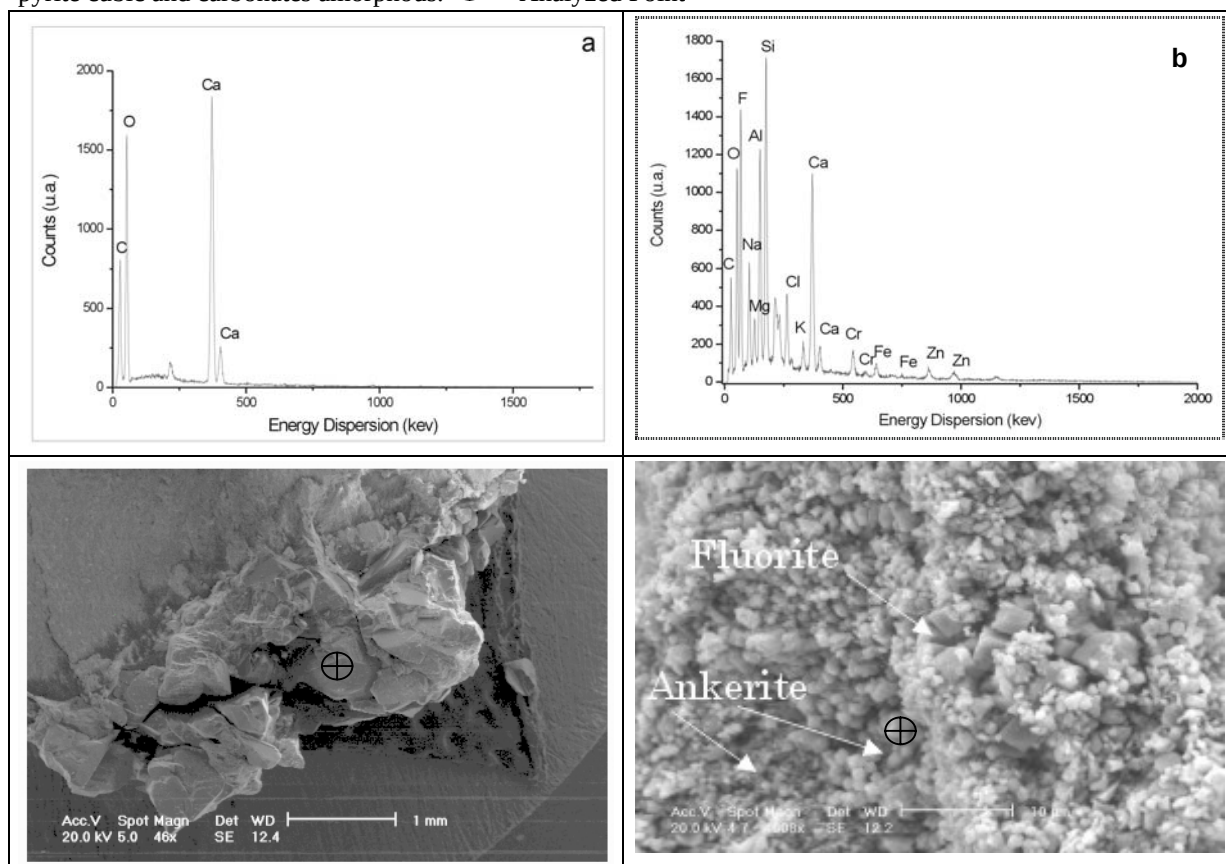


Figure 2(a): EDS characteristic and SEM micrographs of the sample 04-054A (Irati sample) showing the morphology of the calcite crystals. 2(b) EDS characteristic and SEM micrographs of the sample 04-079B (Ponta Grossa) showing fluorite and ankerite crystals. $\oplus$ = Analyzed Point

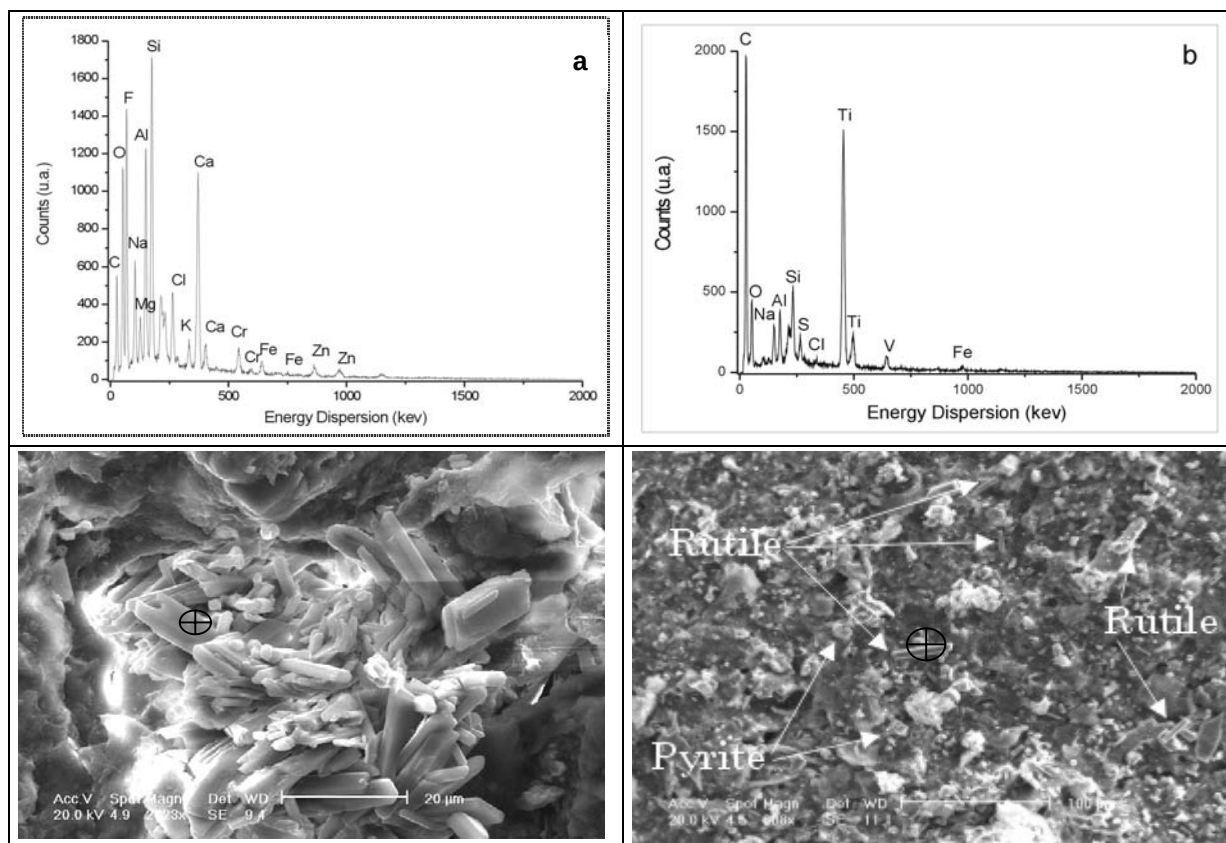


Figure 3(a): EDS characteristic and SEM micrographs in Irati sample 04-049B showing the morphology of the dolomite crystals. 3(b) EDS characteristic and SEM micrographs of the Ponta Grossa sample 04-079B showing Rutile, Pyrite crystals and carbonate amorphous. $\oplus$ = Analyzed Point

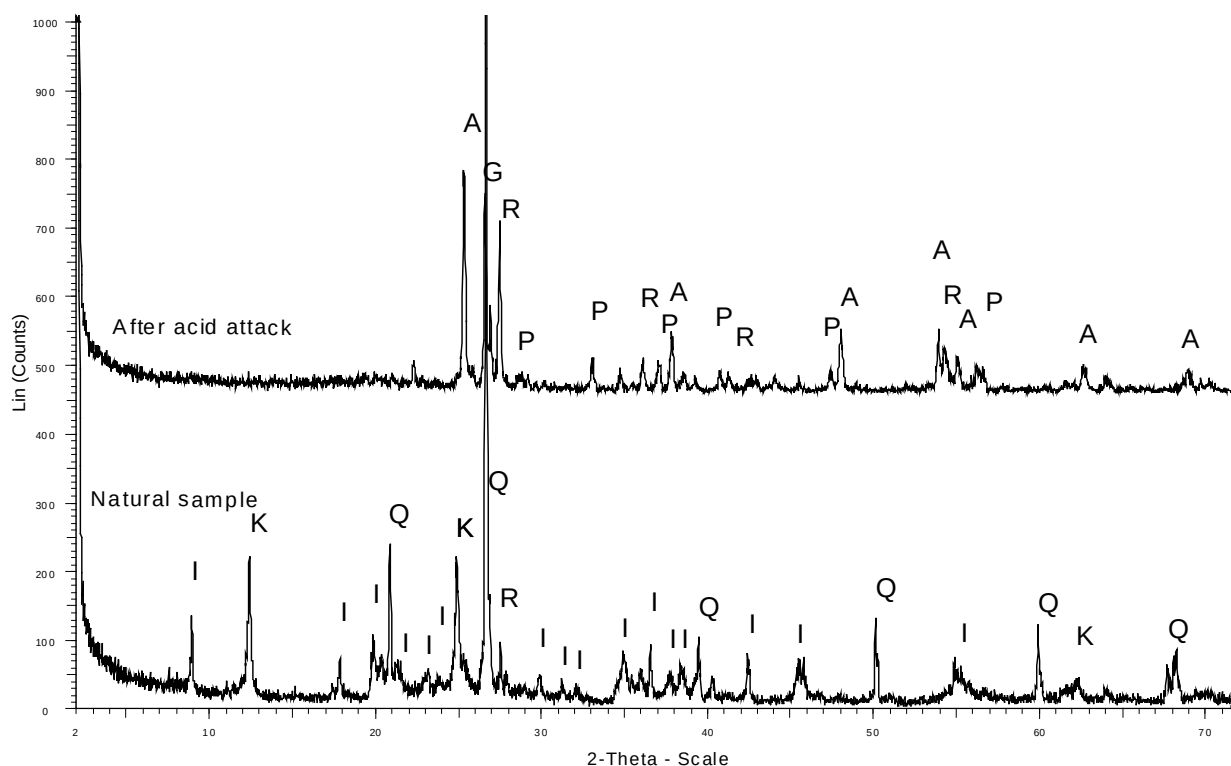


Figure 4: X-ray diffraction patterns of sample 60 after and before acid attack (natural sample). Note that illite, kaolinite and quartz are dissolved with the relative concentration of rutile and pyrite with formation of anatase. I = illite. K = kaolinite. Q = quartz. R = rutile. P = pyrite and A = anatase. This figure shows an example of kaolinite, illite and quartz dissolution with the concentration of rutile, pyrite and formation of anatase and some graphite after acid attack.

5. Acknowledgements

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